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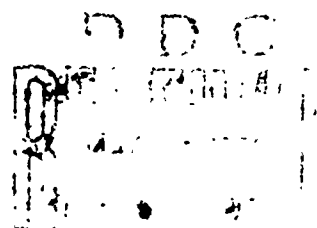
## USAAVLABS TECHNICAL REPORT 67-70

### INVESTIGATION AND ANALYSIS OF AIRCRAFT FUEL EMULSIONS

AD668248

By

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December 1967

**U. S. ARMY AVIATION MATERIEL LABORATORIES  
FORT EUSTIS, VIRGINIA**

**CONTRACT DA 44-177-AMC-445(T)  
MONSANTO RESEARCH CORPORATION  
DAYTON LABORATORY  
DAYTON, OHIO**

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DEPARTMENT OF THE ARMY  
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FORT EUSTIS, VIRGINIA 23604

This report contains the results of investigations of emulsified JP-4 aviation fuel conducted by Monsanto Research Corporation, Dayton, Ohio, under the terms of Contract DA 44-177-AMC-445(T).

The purpose of the program was twofold: (1) to formulate 97 percent internal phase (JP-4) emulsions for laboratory evaluation of their physical, chemical, and rheological properties, and (2) to develop a means of demulsifying these emulsions such that the recovered JP-4 fuel would meet military specification requirements.

The program objectives were met, and two promising emulsion formulations were subjected to extensive laboratory testing. The nature of these tests and the results obtained therefrom are presented in narrative, graphic, and tabular form in this report.

While the fuel emulsion developed under this contract was a first-generation product, data suggest that the use of such fuel in aircraft systems would prove to be most beneficial from the standpoint of reducing the fire hazards associated with aircraft accidents. Consequently, this command has contracted for additional emulsified fuel programs during Fiscal Year 1968. These programs are designed to optimize the promising emulsion formulations developed during the past year, and to further characterize the physical, chemical, rheological, and combustion properties of these fuels. Reports covering these efforts will be available for distribution during the fall of 1968.

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INVESTIGATION AND ANALYSIS OF  
AIRCRAFT FUEL EMULSIONS

Final Report

By

J. C. Harris and E. A. Steinmetz

Prepared by

Monsanto Research Corporation  
Dayton Laboratory  
Dayton, Ohio

for

U. S. ARMY AVIATION MATERIEL LABORATORIES  
FORT EUSTIS, VIRGINIA

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## ABSTRACT

The objective of this contract was the development of flammability-controlled JP-4 emulsions for use in gas turbine engines and recovery of JP-4 from the emulsified fuel for forward base usage. Such emulsified fuels were designed to reduce the probability or intensity of in-flight or postcrash fires. The Alamac emulsion produced under this contract reduced the flame propagation rate to 1/87th that of JP-4 and reduced the area of dynamic burning to 1/6th that of JP-4. Other flame and explosivity tests also showed lower flammability. The emulsion was stable over a -40° to 160°F range, and exhibited no sensitivity to impact, vibration, or gravity acceleration values up to 10,000 g's. Emulsion viscosity met contract requirements, exhibiting yield stress values of about 1300 dynes/cm<sup>2</sup>. Tests with metals and elastomers used in fuel systems showed negligible or low emulsion effect. Lubricity tests showed the emulsion to have a coefficient of friction considerably lower than JP-4 alone. Negligible static charge buildup and high conductivity significantly lowered this potential hazard for the emulsion. Although the emulsion can be pumped satisfactorily, it does not flow freely to a sump. The Alamac emulsion can very readily be broken chemically. The raw recovered JP-4 contains the emulsifier which can be removed quantitatively by filtration through a column of attapulgate clay. Emulsion partially broken by thermal extremes or by multipassage through a centrifugal pump can be reconstituted by mild agitation. Six hundred gallons of the emulsion were produced using a standard formula and procedure.

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## FOREWORD

This program was performed under the authorization of the U. S. Army Aviation Materiel Laboratories under Contract DA 44-177-AMC-445(T), Task 1F121401A14190, and covers the period from 15 June 1966 through 14 June 1967. Contributors under subcontract were the Allison Division of General Motors Corporation, performing the comparative evaluation of the emulsion in the T63 fuel system; the Research Institute of the University of Dayton on emulsion biocidal characteristics; the narrated film documentation by Patterson Presentations, Dayton, Ohio; and impact and vibration tests by Bowser-Morner Testing Laboratories, Inc., Dayton, Ohio. We acknowledge with thanks the courtesy extended by the DeLaval Company in permitting use of their Gyro Tester Centrifuge.

The consultation and guidance given by Mr. W. J. Nolan, Captain S. S. Pelosi, Jr., and Captain G. W. Bowling of the Aviation Materiel Laboratories have been most helpful and appreciated.

Monsanto Research Corporation personnel who contributed to this effort were R. A. Anduze, G. L. Ball III, E. L. Brown, J. R. Gibson, G. L. Hanna, D. L. Harris, C. J. Huffman, M. F. Johnston, C. E. Lowe, J. R. McKendree, R. G. Olt, R. E. Pence, D. L. Plessinger, W. G. Scribner, and E. A. Steinmetz under the direction of Jay C. Harris, the project director.

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## INTRODUCTION

The main objective of this work was the development of emulsions of JP-4 which, while combustible, reduced the uncontrolled burning properties of JP-4. The practical significance of reduced flammability is reduction in intensity and rate of propagation of in-flight or postcrash fires. Desired was a product capable of being burned directly in gas turbine engines or from which could be recovered specification quality fuel at a forward base. To achieve these ends, it was permissible to provide an emulsion of either end use, or preferably to formulate a single emulsion providing both capabilities.

The contractual work statement comprised two phases: Phase I, a literature search and an optimized method for selection of emulsifiers and external phase materials; and Phase II, performance tests of the selected emulsions, their preparation and recovery, and properties of the fuel recovered from the selected emulsion.

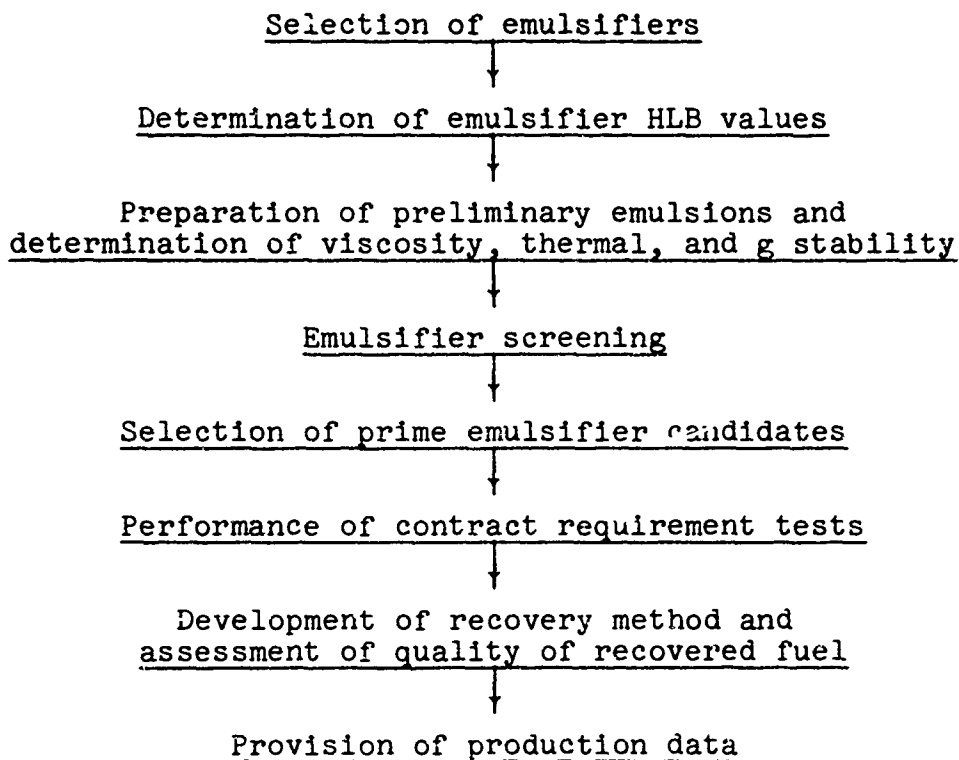
The program as originally conceived was based upon the following assumptions: (1) that mixtures of emulsifiers would be required to provide the necessary emulsion characteristics, (2) that optimization of the emulsifier mixtures would be necessary, and (3) that viscosity modifiers might be required. Following this portion of the program, secondary screening, fuel recovery, and quality assessment were conceived as the next steps.

Fluids to be used as the outer phase depend upon several requirements: They obviously should not be flammable and, in fact, must depress the volatility of the fuel to reduce flammability. Such fluids should be mobile, consumable at engine combustion temperatures, and remain fluid at low temperatures. An additional requirement is that the emulsifiers be soluble in the outer phase fluids and, for nonionic surfactants, that they permit hydrogen bonding. Water is an obvious candidate, and an organic liquid meeting the foregoing requirements is ethylene glycol (EG). A mixture of equal parts of deionized water and EG has a freezing point of  $-40^{\circ}\text{F}$ , and since low-temperature stability is required, the EG/water mixture appeared a reasonable starting point.

Since there are literally hundreds of potentially suitable emulsifiers, some means for categorizing them and selecting those most suitable was required. Chosen was a hydrophile-lipophile balance (HLB) technique, since this ratio indicates the potential solubility of the emulsifier in water or oil

(the higher the HLB value, the more water soluble). Needed to supplement the HLB values was a method to determine whether chosen HLB values in fact would produce emulsions. A very simple procedure was established, and the relative degree of thermal stability was determined.

This preliminary data indicated that single emulsifiers provided stable emulsions at a 97% JP-4 internal-phase concentration. This meant that the actual program had the following structure:



The data given in the main body of this report will show the preferred methods and the data secured with them. Other relevant test data are cited in appropriate appendixes.

### DEVELOPMENT OF PROBLEM

Phase I consists of a literature search concerning high internal-phase emulsions, particularly those of oil-in-water (o/w) emulsions with hydrocarbon fuels. The survey showed this to be a new technological area, with very little data available. Another portion of this phase was the development of a laboratory screening procedure to optimize the evaluation of potential emulsifiers and emulsions prepared from them. The procedure ultimately followed, and considerably shortened, is described in more detail in the Introduction. The initial portion of Phase II consisted of emulsifier screening tests, which led to the selection of several prime emulsifier candidates, thermally stable and gravity-acceleration stable, and of the desired viscosity level.

Following the preliminary evaluation, two candidate emulsions, named for the emulsifiers Emcol CS-136 and Alamac H26D, were subjected to other property and characteristics tests required by the contract. Early attempts at the preparation of multi-gallon quantities of the emulsions revealed that during manufacture, the Emcol emulsifier was sensitive to temperatures lower than 75°F, resulting in incomplete JP-4 emulsification. Resorting to the remaining Alamac emulsion candidate resulted in the successful manufacture of the required 600 gallons of emulsion. The remaining contract requirement tests were then performed using the Alamac emulsion. This emulsion met the quality requirements as described in the body of this report and, additionally, permitted the development of an effective recovery system for JP-4.

Furthermore, it was found that an emulsion partially separated as a result of excessive thermal or shear exposure could be reconstituted by mild agitation.

## EXPERIMENTAL DATA AND DISCUSSION

### PART I. LITERATURE SURVEY AND METHOD OF EMULSIFIER SELECTION

The several objectives of this survey are to identify available emulsifiers and continuous phase materials, and to develop and apply a method of selection based upon recent techniques in order to minimize the number of emulsifiers and continuous-phase materials to be tested.

The results of the literature survey and a summary of the method used for emulsifier selection follow. The entirety of Part I is included as Appendix I.

A review was made of the pertinent literature concerned with high-internal-phase JP-4 emulsions. This review indicates that these emulsions represent a quite new technology which has as yet received comparatively little attention.

Discussed are the emulsifiers to be tested, their chemical and use properties, initial candidates, and a method for their selection. External-phase and viscosity modifier component requirements are defined and candidates discussed.

Given are the initially proposed methods of emulsifier selection and screening based on the theory that emulsifier mixtures would be required. A revised and much simplified method for selection and screening is given, because single emulsifiers perform quite satisfactorily.

### PART II. EMULSIFIER SELECTION

(During the course of the contract research, Parts II-V were done as "Phase II" of the subject contract.)

#### 1. Preliminary Emulsifier Selection

##### 1.1 General

Emulsifiers are materials particularly selected for their capability of aiding in and maintaining emulsion formation. They more generally are called surfactants, since they are surface active agents; these terms may occur interchangeably herein.

The following general types of surfactants are available and are categorized according to the terminal groups which impart water solubility:

Anionics (frequently as  $\text{SO}_3^-$  or  $\text{SO}_4^-$ )

Cationics ( $\text{OH}^+$  or  $\text{Cl}^+$ , etc.)

Nonionics (ether linkages and terminal OH)

Amphoterics ( $\text{NH}^+$  and  $\text{COOH}^-$  in same molecule)

Another class of recent origin is phosphate esters containing nonionic linkages.

All of these surfactants contain a lipophilic group of variable carbon-chain length with a corresponding hydrophilic group. Choice of lipophile length and/or structure can markedly affect the type and stability of emulsion, and can further be chosen for optimum utility with the specific lipophile internal emulsion phase. Previous emulsion experience indicated that the most likely lipophiles for the immediate purpose would be straight chains of at least 12 carbons, and preferably 18 carbons, in length. Based on this and the surfactant type as criteria, commercially available agents were selected from McCutcheon's<sup>1</sup> annual, and these were secured from the suppliers. Listed in Appendix II are the surfactants tested and their compositions.

Since the ash contributed by the emulsifier must be minimized, it was not possible to use the frequently available sodium or potassium salts, but instead the unneutralized acids were obtained and neutralized with amines, particularly triethanolamine (TEA). Other amines were tested, as indicated below, in greater detail.

The emulsifiers, comprising the broad spectrum of types commercially available, were chosen for evaluation with the objectives of determining relative capability, types most applicable, and prime candidates. Since length of lipophile side chain and variation in ethylene oxide (or polyglycol) or hydrophile type and content so sharply affect the HLB and emulsifying values, representative homologous series of the various agents were selected for tests.

## 1.2 HLB Determination and Values

Considerable previous experience with emulsifiers for agricultural emulsions, comprising petroleum distillate solutions of the active insecticidal or herbicidal agent, indicated that optimum results were obtained with mixtures of anionic

and nonionic emulsifiers. It was expected, therefore, that combinations of surfactants might prove necessary and, if so, that a statistical approach to minimize efforts would be needed. Such an approach was described in Phase I, using hydrophile-lipophile balance values.

Emulsions of this type at least, i.e., o/w, comprise a skin or pellicle of external phase in which the emulsifier distributes itself between the oil and water phases, the hydrophile end in water and the lipophile end toward or in the oil phase. The ratio between these phases is known as the hydrophile-lipophile balance. A preliminary indication of emulsifier quality then consisted in the HLB value determination.

Griffin<sup>2</sup> devised the HLB method, which has been used relatively effectively for some time. One difficulty with its use is that precise analytical data are needed to arrive at the numerical HLB value. Another, simpler approach was sought.

Realizing the frequent lack of the necessary analytical data, Griffin<sup>3</sup> developed an arbitrary technique showing ranges of HLB based upon emulsifier water solubility:

<u>Behavior When Added to Water</u>	<u>HLB Range</u>
No dispersibility	1-4
Poor dispersion	3-6
Milky dispersion after vigorous agitation	6-8
Stable milky dispersion (upper end almost translucent)	8-10
From translucent to clear dispersion	10-13
Clear solution	13+

While less precise than the analytical or tedious blending technique, this procedure served to screen surfactant candidates.

The method used is as follows: Each surfactant is weighed in 1.0-gram amounts into 200-ml Erlenmeyer flasks. Distilled water in 99-ml volumes is added, and the flasks are stoppered and shaken vigorously. Mixtures may be warmed, but are observed at  $75 \pm 5^{\circ}\text{F}$ .



As an assessment of the method, a series of Atlas products of published HLB values was prepared, and comparative values show the applicability of the method.

<u>Surfactant</u>	<u>Published HLB Value</u>	<u>Range by Water Solubility</u>
Span 65	2.1	1-4
G 3570	4.5	3-6
Span 40	6.7	6-8
Tween 61	9.6	8-10
Brij 56	12.9	10-13
Tween 20	16.7	13+

The literature indicates that an HLB value of about 12.5 is a near optimum for emulsions of hydrocarbons of the nature of JP-4. Since HLB or a value correlatable with it seems the more direct approach, surfactants of HLB 12.5 (or equivalent) were tested initially. A few of lower value were included to verify the selection.

Table I records the HLB values for most of the 69 emulsifiers tested. The constitutions of these emulsifiers are given in Appendix II.

## 2. Preparation of Preliminary Emulsions

### 2.1 Emulsion Screening

#### 2.1.1 General

Mechanical agitation required for emulsion preparation in general has been of many types; e.g., propellor, kneading, impingement, ultrasonic, etc. The type used depends considerably upon the emulsion constituents and the desired final emulsion characteristics. Emulsions in which the internal phase comprises from a few percent to about half the formulation may frequently be manufactured in whichever of several types of equipment are available or fit into a process stream.

Preliminary emulsification trials were made using a Hobart Kitchen Aid mixer with the wire strip stirrer at a 95 fuel/5 external-phase ratio. The 5% external phase was composed of water, 2 vol %; ethylene glycol, 2 vol %; and emulsifier, 1 wt %; respectively, on the formula basis. This

TABLE I. EMULSION DATA

TABLE I. EMULSION DATA													
30-cc Fuel Emulsion Preparations; 800 cc Batches, 1/2% Internal Phase, Fuel Phase Added to Water Phase in Small Quantities.													
No.	Surfactant	External Phase		No. Days	Stability		Apparent Viscosity (7 Spindles at 100 RPM)				Centrifuge 500 g 30 min.		
		Wt. % Surf.	Vol. % H <sub>2</sub> O		1 Day	7 Days	2	4	10	20			
1	Ceraquat 303	0.6	1.2	1.2	5 min	2 phase in 5 min.							8-10
2-1	Armac T	0.3	1.5	1.35		N.C.	2 phase	168	85	42	24	N.C.	10-13
2-2	Armac T	0.50	1.25	1.25		N.C.	8% fuel	55	35	18	12		
3	Bucol N-50	0.3	1.37	1.37	1 day	N.C.	2 phase	30	20	10	6		12-13
4	Ignopal DM 430	0.3	1.37	1.37		No gel formed							8-10
5	Brij 96	0.3	1.37	1.37		No gel formed							12-9
6	Span 40	0.3	1.38	1.38		No gel formed							6-7
7	Sterox AS-100	0.3	1.38	1.38	2 days		N.C.	2 phase					13+
8	Sterox D3	0.3	1.38	1.38			N.C.	2 phase					13+
9	Sterox D7	0.3	1.38	1.38		No gel formed							8-10
10	Sterox W	0.3	1.38	1.38		No gel formed							13+
11	OS Silicone 20 1065	0.3	1.38	1.38		Slight gel formed at first							13+
12	Pluronic L 31	0.3	1.38	1.38		No gel formed							13+
13	Pluronic L 62	0.3	1.38	1.38		Good gel at first, not all fuel went in							13+
14	Pluronic L 63	0.4	1.25	1.31		Gel formed at first, not all fuel went in							13+
15	Pluronic L 101	0.3	1.38	1.38	2 days	No gel formed							8-10
16	Ammonyx 856	0.3	1.38	1.38		Gel formed only at first							13+
17	Emurest 2640	0.3	1.38	1.38		Gel formed only at first							8-10
18	Emurest 2642	0.3	1.38	1.38		Gel formed only at first							8-10
19	Emurest 2648	0.3	1.38	1.38		Gel formed only at first							8-10
20-1	Deriphant 151C	0.3	1.37	1.37		2 phase	2 phase						
20-2	4% Deriphant 151C	0.65	0.97	1.37	1 hr only	Did not last as long as with smaller concentration of surfactant.							
21-1	Deriphant 170C	0.3	1.37	1.37		2 phase	2 phase						
21-2	50% Deriphant 170C	0.60	1.06	1.37	1 week	N.C.	100% sep'n						
22-1	Alamc M55	0.3	1.37	1.37		N.C.							10-13
22-2	Alamc M56 - 1600 cc	0.3	1.37	1.37		N.C.							
22-3	Alamc M56 - 6400-cc batch	0.30	1.37	1.37		N.C.							
22-4	Alamc M260	0.50	1.25	1.25		N.C.							
22-5	Alamc M55	0.30	0	2.70		N.C.							
22-6	Alamc M56	0.30	0.68	2.05		N.C.							
23-1	Alamc 21D	0.3	1.37	1.37	1 day	Sloppy gel formed and separated overnight.							
23-2	Alamc 21T	0.50	1.25	1.25	2 hr	Test failed.							
24-1	Omco K	0.6	1.2	1.2									
24-2	Omco K	0.3	1.5	1.38		N.C.	2 phase						13+
25-1	Omco JCE	1.0	1.0	1.0	5 min	Gel lasted only 5 min.							13+
25-2	Omco D2N	0.6	1.2	1.2	5 min	Gel lasted only 5 min.							13+
25-3	Omco D2N	0.3	1.5	1.35		Gel wouldn't accept all fuel.							
26-1	Bucol N-50A	0.4	1.25	1.31		Gel wouldn't accept much fuel							10-13
26-2	Bucol N-50C	0.3	1.38	1.38	2 days		N.C.	2 phase					

No.	Surfactant Name	External Phase Vol.-%		Stability	Apparent Viscosity (# Spindles)				Centrifuge 500 g 30 Min.	HLB Value
		Water	Styrene		1 Day	7 Days	1 Day	7 Days		
D 28000	D 28000	0.6	1.20	Synopsis	2 phase	35	10	2	15+	
D 28000	D 28000	0.4	1.25	2 phase	2 phase	70	45	26	15	
D 28000	D 28000	0.3	1.38	Gel formed - only accepted 500-cc fuel					M.C.	
Katapol PM 430	Katapol PM 430	0.4	1.25	No gel formed					13+	
Katapol PM 430	Katapol PM 430	0.3	1.38	Gel formed only at first					13+	
Emulphor ON 870	Emulphor ON 870	0.4	1.25	2 phase	2 phase	202	107	52	32	
Emulphor ON 870	Emulphor ON 870	0.3	1.38	2 phase	2 phase	140	94	44	25	
Primalox R-15	Primalox R-15	0.4	1.25	2 phase	2 phase				M.C.	
Primalox R-15	Primalox R-15	0.3	1.38	No gel formed					M.C.	
Primalox T-5	Primalox T-5	0.4	1.25	2 phase	2 phase				13+	
Primalox T-5	Primalox T-5	0.3	1.38	No gel formed					13+	
Primalox T-15	Primalox T-15	0.4	1.25	2 phase	2 phase				17-9	
Primalox T-15	Primalox T-15	0.3	1.38	Gel formed only at first - wouldn't take all fuel.					13+	
Nyrj 53	Nyrj 53	0.4	1.25	Gel formed only at first - wouldn't take all fuel.					15-7	
Nyrj 53	Nyrj 53	0.3	1.38	Gel formed only at first - wouldn't take all fuel.					13+	
Dow Corning 113	Dow Corning 113	0.4	1.25	Gel formed only at first - wouldn't take all fuel.					15-7	
Dow Corning 113	Dow Corning 113	0.3	1.48	Gel separated after 5 min.					13+	
B-1J 58	B-1J 58	0.3	1.32	2 phase	2 phase	160	110	52	29	
B-1J 58	B-1J 58	0.3	0	2 phase	2 phase				M.C.	
Calsoft LAS 99	Calsoft LAS 99	0.3	1.38	Gel formed only at first					M.C.	
LAS 99 + N-propylene	LAS 99 + N-propylene	0.4	1.25	Gel separated at R.T. for 1 hr					M.C.	
LAS 99 + TEA (amine)	LAS 99 + TEA (amine)	0.4	1.31	M.C.	2 phase	88	42	59	46	
Stearic acid + TEA	Stearic acid + TEA	0.4	1.25						M.C.	
Above emulsion "in situ"	Above emulsion "in situ"	0.4	1.25	Gel separated overnight					M.C.	
Oleic acid + TEA	Oleic acid + TEA	0.4	1.31	Synopsis	2 phase	10	5	4	0	
Oleic acid + N-propylene	Oleic acid + N-propylene	0.3	1.37						M.C.	
Gafac RM-410 + N-propylene	Gafac RM-410 + N-propylene	0.4	1.25	Gel formed but only accepted 400-cc fuel.					M.C.	
Above with glycol substitute	Above with glycol substitute	0.4	1.25						M.C.	
Gafac RM-410 + N-propylene	Gafac RM-410 + N-propylene	0.4	1.30	M.C.	M.C.	70	45	22	13	
1600 cc	1600 cc	0.4	1.30						M.C.	
Gafac RM-410 + TEA	Gafac RM-410 + TEA	0.4	1.30						M.C.	
Antara LP-200 + TEA	Antara LP-200 + TEA	0.4	1.25						M.C.	
Above in 1600-cc batch	Above in 1600-cc batch	0.4	1.25						M.C.	
Antara LP-200 - 1600 cc	Antara LP-200 - 1600 cc	0.4	1.30						M.C.	
At once	At once								M.C.	
1 day	1 day								M.C.	
Antara LP 200 + TEA	Antara LP 200 + TEA	0.4	1.30	Hobart Model C-100 mixer, emulsion formed easily at No. 2 speed.					M.C.	
Tween 20	Tween 20	0.3	0	Synopsis	2 phase				M.C.	
Tween 20	Tween 20	0.3	1.38						M.C.	
Tween 20 - 1600 cc	Tween 20 - 1600 cc	0.3	1.37						M.C.	

TABLE I - Continued

No.	Surfactant Name	External Phase		Stability	Apparent Viscosity		Centrifuge
		Vol. % Surf.	Vol. % H <sub>2</sub> O	1 Day	1 Day	1 Day	500 g 30 Min.
43-1	Emul CS-141 + TEA	0.3	1.37	1.37	1.37	1.37	13*
43-2	Above prepared "in situ"	0.3	1.37	1.37	1.37	1.37	
43-3	Emul CS-141 + TEA (correct amount of TEA)	0.3	1.37	1.37	1.37	1.37	
43-4	Emul CS-141 - No TEA	0.3	1.37	1.37	1.37	1.37	
43-5	Tween 60	0.3	1.38	1.38	1.38	1.38	
43-6	Tween 60	0.3	0	2.75	2.75	2.75	
43-7	Tween 60	0.3	1.38	1.38	1.38	1.38	
43-8	Tween 60	0.3	1.37	1.37	1.37	1.37	
43-9	1000 cc 1:1:1:1 Mixer	0.3	1.37	1.37	1.37	1.37	
44-1	Tween 60 - Glycerine	0.3	1.37	1.37	1.37	1.37	
44-2	Tween 60 - Propylene Glycol	0.3	1.37	1.37	1.37	1.37	
44-3	Tween 60 - Diethylene Glycol	0.3	1.37	1.37	1.37	1.37	
44-4	Tween 60 - Dipropylene Glycol	0.3	1.37	1.37	1.37	1.37	
44-5	Tween 60 - Carbowax 300	0.3	1.37	1.37	1.37	1.37	
44-6	Tween 60 - Carbowax 300	0.3	0	2.75	2.75	2.75	
44-7	Tween 60 - Methanol	0.3	1.37	1.37	1.37	1.37	
44-8	Tween 60 - 1600 cc	0.3	1.37	1.37	1.37	1.37	
44-9	Tween 60 - 1600 cc	0.3	1.37	1.37	1.37	1.37	
44-10	Tween 60 - 1600 cc	0.3	1.37	1.37	1.37	1.37	
45-1	Antara LE-600 + N-propylamine	0.4	1.25	1.31	1.31	1.31	
45-2	Antara LE-600 + TEA	0.4	1.31	1.31	1.31	1.31	
45-3	Antara LE-600 + TEA - 1600 cc	0.4	1.31	1.31	1.31	1.31	
45-4	LE-600 + Homolepropylamine	0.4	1.31	1.31	1.31	1.31	
45-5	LE-600 + 2 Amino-1-butanol	0.4	1.31	1.31	1.31	1.31	
45-6	Antara LE-600 + TEA - 1600 cc After 1 week	0.3	1.27	1.37	1.37	1.37	
45-7	LE-600 + 2 ethylaminoethanol	0.4	1.30	1.30	1.30	1.30	
45-8	LE-600 + Isopropanolamine	0.4	1.30	1.30	1.30	1.30	
45-9	Antara LE-600 + TEA - 1600 cc	0.4	1.30	1.30	1.30	1.30	
45-10	Antara LE-600 + TEA	0.4	0	2.60	2.60	2.60	
46-1	Emul CS-136 + TEA	0.3	1.37	1.37	1.37	1.37	
46-2	As above, adding last 676-cc fuel in plug	0.3	1.37	1.37	1.37	1.37	
46-3	As above, adding all 776-cc fuel in plug	0.3	1.37	1.37	1.37	1.37	
46-4	Emul CS-136 Dispersion Mixer	0.3	1.37	1.37	1.37	1.37	
46-5	As above with all 776-cc fuel in plug	0.3	1.37	1.37	1.37	1.37	

TABLE I - Continued

No.	Surfactant Name	External Phase		H <sub>2</sub> O Temp. 30 Days	Stability		Apparent Viscosity #7 Spindles (Cgs x 10 <sup>3</sup> )		Centrifuge 500 g 30 Min.	HLB Value
		Wt. % Surf.	Vol. % H <sub>2</sub> O		1 Day	7 Days	1 Day	7 Days		
46-6	Emcol CS-136 + TEA (corrected amount of TEA)	0.3	1.37	1.37	N.C.	N.C.	N.C.	N.C.	N.C.	
46-7	Emcol CS-136 + TEA (corrected) 1600 cc	0.3	1.37	1.37	N.C.	N.C.	N.C.	100 100 76 74		
46-8	Emcol CS-136 - No TEA	0.3	1.37	1.37	CS-136 formed a gel with H <sub>2</sub> O and glycol - broke down when JP-4 was added.					
46-9	Emcol CS-136 + TEA - 1600 cc repeat	0.3	1.37	1.37	N.C.	N.C.	N.C.	170 150 102 84		
46-10	Emcol CS-136 + TEA 3200-cc batch	0.3	1.37	1.37	Hobart Model C-100 mixer, emulsion formed easily at No. 2 speed.					
46-11	Emcol CS-136 + TEA 6400-cc batch	0.3	1.37	1.37	Hobart Model C-100 mixer, emulsion formed easily at No. 2 speed.					
46-12	Emcol CS-136 + TEA	0.3	0	2.74	1% Fuel	10% Fuel	20% Fuel			
46-13	Emcol CS-136 + TEA	0.3	0.68	2.05	Good sticky gel - only 700 cc of fuel went in.					15.7
47	Brij 58 - 0.1% Polyox WSR 205	0.3	1.30	1.30	No gel formed.					8
48	M-Cocoyl-hydroxy butyramide	0.3	1.37	1.37	N.C.	N.C.	Synersia 6 drops fuel	130 95 58 38	N.C.	13+
49	Emcol CS-131 + TEA	0.3	1.37	1.37	N.C.	N.C.	N.C.	120 95 60 47	N.C.	13+
50-1	Emcol CS-140 + TEA	0.3	1.37	1.37	N.C.	N.C.	N.C.	140 115 82 56		13+
50-2	Emcol CS-140 + TEA	0.3	1.37	1.37	Hobart Model C-100 mixer, emulsion formed easily at No. 2 speed.					
51	Emcol CS-151 + TEA	0.3	1.37	1.37	N.C.	N.C.	2 phase			
52-1	Solid Acetamide	qual	none	none	Hand mixing, fuel added to acetamide produced no gel.					
52-2	80% Acetamide in Water	qual	none	none	Hand mixing, fuel added slowly - no emulsion.					
52-3	50% Acetamide in Water	(ca. 1.5	1.5		Kitchen Aid, normal fuel addition - no emulsion.					
52-4	52-3 + Tween 60	0.3	1.37	1.37	N.C.	N.C.	N.C.	20 15 9 8	Kitchen Aid	
53-1	Emcol CS-136 + TEA & Acetamide	0.3	1.37	1.37	N.C.	N.C.	N.C.	75 60 42 27	N.C.	
53-2	Liquid Formamide	1.0	0	0	Kitchen Aid, no gel or emulsion formed.					
53-3	50% Formamide in Water	1.5	1.5	0	Kitchen Aid, no gel or emulsion formed.					
53-4	53-2 + Tween 60	0.3	1.37	1.37	Shaking would not break it.	N.C.	Shaking would not break it.	40 35 26 18	Kitchen Aid	
53-5	Tween 60 & Formamide 1600-cc batch	0.3	1.37	1.37	N.C.	N.C.	N.C.	25 17 7 4		
54-1	Emcol CS-130 + TEA & Formamide	0.3	1.37	1.37	N.C.	N.C.	N.C.	35 30 21 15		
54-2	Propionamide	Alm - 1.0			Amide was solid and wouldn't dissolve in fuel - no gel.					
54-3	80% in Water	Alm - 1.0			Dissolved in water but recrystallized when fuel was added.					
54-4	5% in Water	Alm - 3.0			Stayed dissolved but would not emulsify.					
54-5	40% Arsenic 72	0.3	1.37	1.37	1-cc fuel	N.C.	Synersia	25 17 8 5		13+
54-6	40% Arsenic 72	0.75	0.9	1.37	Test failed.					
54-7	40% Arsenic 72	0.3	1.37	1.37	5-cc fuel	N.C.	15.0% of free fuel	15 7.5 2 1		10-13
54-8	40% Arsenic 72	0.3	1.37	1.37	N.C.	2 phase	2 phase	30 15 9 4		
54-9	40% Arsenic 72	0.75	0.9	1.37	No gel formed.					
54-10	30% Arsenic 72	0.3	1.37	1.37	10% - 2 phase	N.C.	N.C.	20 8 2 0.5		13+

TABLE I - Continued

No.	Surfactant Name	External Phase		Re. Temp. 30 Days	Stability		Apparent Viscosity #7 Spindle (cpa x 10 <sup>-3</sup> )				Centrifuge 500 g 30 Min.	HLB Value
		Wt. % Surf.	Vol. % Et. Glycol		1 Wk.	7 Days	1 Day	1 Day	1 Day	1 Day		
59-1	30% Ammonyx LO	0.3	1.37	1.37	1 hr							13+
59-2	30% Ammonyx LO	1.0	0.65	1.37	1 hr							13+
60-1	30% Ammonyx CO	0.3	1.37	1.37								
60-2	30% Ammonyx CO	1.0	0.65	1.37	2 hr							
61	Escol CS-187 + TEA	0.3	1.37	1.37								
62-1	As 53-5, but as much fuel added as possible	0.15	0.63	0.68								
62-2	As 62-1 at point before breakdown	0.15	0.68	0.68								
62-3	As 53-5, but glycol instead of formalde	0.18	0.81	0.81								
62-4	As 62-3 at point before breakdown	0.20	0.90	0.90								
62-5	Antara LE-600 + TEA, 2% external phase	0.20	0.93	0.93								
62-6	Escol CS-136 + TEA	0.10	1.45	1.45								
62-7	Escol CS-136 + TEA	0.20	1.42	1.42								
62-8	Escol CS-136 + TEA 2.5% external phase	0.25	1.11	1.11								
62-9	Escol CS-136 + TEA & Formalde 2% external phase	0.20	0.93	0.93								
62-10	Antara LE-600 + TEA 2% external phase	0.20	0.93	0.93								
62-11	Escol CS-136 + TEA	0.15	1.43	1.43								
63	55% Armeen Z	0.55	1.12	1.37								
64-1	Escol CS-140 + TEA & Alamac H2C <sub>4</sub>	0.30	1.37	1.37								
64-2	Escol CS-136 + TEA & Alamac H2C <sub>4</sub>	0.30	1.37	1.37								
65	Formoxite 801	0.30	1.37	1.37								
66	Duomeen C	0.30	1.37	1.37								
67	Duomeen T	0.30	1.37	1.37								
68	Ethomid HT/15	0.30	1.37	1.37								
69-1	Ethomid HT/60	0.30	1.37	1.37								
69-2	Ethomid HT/60	0.50	1.25	1.25								

\* Collapsed

† Glycine

‡ 40% excess TEA than needed for pH 9.5

§ 2nd viscosity was taken after emulsion was re-formed

¶ Viscosity reading taken 1 week after emulsion formed

⌋ Small amount of free fuel on top

⌋ Broke on stirring cold

⌋ 40% excess TEA

ratio was chosen since it approached the 97/3 ratio specified, and would permit variation in either direction, depending upon the emulsion results obtained.

Nine surfactants (and their HLB values) that failed to produce an emulsion or a gel under the above conditions were:

<u>Surfactant</u>	<u>Composition</u>	<u>HLB</u>
Actiflo 70-UB	Natural lecithin	1-4
Adol 63	Hydrogenated tallow alcohol	1-4
Adogen 363	Tertiary trilaurylamine	3-6
Adogen 160	Primary coco amine	8-10
Alkaterge C	Substituted oxazoline	3-6
Alrodyne 315	Polyethylene glycol fatty ester	13+
Armeen T	Primary tallow amine	8-10
Brij 56	Polyoxyethylene(10)-cetyl ether	12.9
Cardene	N,N-bis(hydroxyethyl)-oleamide	8-10

The nine surfactants that failed to produce gels under these conditions tended to conform to the requirement that HLB values be 12 or above, with two exceptions. Exceptions are also apparent in Table II, but those which were successful tended to conform. An apparent "rule of thumb" appears to be that the HLB value for these emulsifiers, as tested by the dispersibility measure, should be 13+.

Having proved that emulsions could in fact be prepared at the 95/5 ratio, further emulsion evaluation was made only at the 97/3 volume ratio. Strictly speaking, the emulsior test could be used as the emulsifier capability screener without regard to HLB value, but if this is already known, and is below 8-10, no further testing is required.

These fuel emulsions differ markedly from most, and in a sense, represent a new technology. Emulsifying 97 vol % of a hydrocarbon in 3-vol % external phase is unusual and presents a number of problems. One of these is that the external phase should be maintained during manufacture. Another problem is that the starting point of 3 vol % of the formulation requires a mixer which can start operations at this low

TABLE II. STABILITY, VISCOSITY, AND g-LOAD TESTS ON EMULSIONS										
External Phase: 1.0 wt.% surfactant, 2.0 vol.% water, 2.0 vol.% ethylene glycol										
Surfactant	Stability at -20°F 1 Day	Stability at -20°F 7 Days	Stability at 135°F 1 Day	Stability at 135°F 7 Days	2-6 rpm	4-12 rpm	10-30 rpm	20-60 rpm	g-load 500 g	HLB
D 28000	N.C.	N.C.	N.C.	N.C.	26,960	16,360	8,160	4,660	N.C.	13+
Armeen Z	2 phase	-	2 phase	-	-	-	-	-	-	13+
Armac T	N.C.	N.C.	N.C.	N.C.	60,160	35,460	15,360	8,920	N.C.	8-10
Amidox C-2	N.C.	-	2 phase	-	-	-	-	-	-	10-13
Amidox C-5	N.C.	-	2 phase	-	61,610	30,810	14,350	8,490	-	13+
Cerasynt 303	N.C.	-	2 phase	N.C.	160,000	103,000	21,800	23,000	2 phase	8-10
Conco DCS	N.C.	N.C.	N.C.	N.C.	278,000	157,000	67,600	35,600	N.C.	13+
Conco K	N.C.	N.C.	N.C.	2 phase	131,000	77,500	33,600	18,500	N.C.	13+
N.C. - No change										
*First three viscosities taken with #4 spindle at 6, 12, 30, 60 rpm. Last three viscosities taken with #7 spindle at 2, 4, 10, 20 rpm.										



level, yet be of such capacity that an extremely viscous fluid can be worked adequately.

Preliminary examination of mixers, with emulsions found satisfactory in the Hobart machine, showed that the Lightning propellor-type mixer (Table I, Test 43-5), even at quite low speeds, failed to mix adequately at the later stages of emulsification. Similar difficulties were experienced with Premier's Dispersator mixer (Test 43-4). Uniformly excellent results were obtained with a Hobart Kitchen Aid mixer (either 1/2-gallon or 2-gallon size), which gives slow-speed planetary agitation with the agitator blades revolving opposite to the direction of head revolvment. The only piece of full-scale equipment reproducing this action is a Day Pony Mixer with 100-gallon maximum capacity. A laboratory-scale mixer of this type produced a satisfactory emulsion. Large-scale preparation is discussed in a later section.

#### 2.1.2 Batch Preparation

A typical batch preparation used for screening emulsifiers follows:

Mixer - Hobart Kitchen Aid (Models K4-B and 100-C)  
(800-ml volume for K4-B)

Batch - (1) Emulsifier 0.3 wt %  
(2) Deionized water 1.37 vol %\*  
(3) Ethylene glycol 1.37 vol %\*  
(4) JP-4 97 vol %

\*Note - Contraction in volume, so that 1, 2, and 3 give 3 vol %.

- Mixing - (A) Dissolve emulsifier in water-glycol mixture.
- (B) Transfer (A) to mixer bowl, agitate at slow speed, and add JP-4 slowly until an emulsion forms. This will take about 10% of the fuel.
- (C) Continue adding JP-4 (either continuously or as small additions), maintaining the external o/w emulsion. If an excess of fuel is added at or near the 50% addition level, a rubbery gel is formed which must be worked smooth before further fuel is added. The rubbery stage can be prevented by controlled fuel addition.
- (D) After all the fuel is added, continue agitation until a characteristic smooth consistency is attained. Mixing is terminated at this stage.

### 3. Preliminary Emulsion Evaluation Tests

These tests were very easily made and comprised storage stability at ambient (77°F) conditions for 30 days; thermal stability for a week at -20° and 135°F; apparent viscosity by Brookfield viscometer; and exposure at 500 g for 30 minutes (ASTM D 96). These data are shown in Table I.

#### 3.1 Emulsifier Screening

Probably the best-known general class is the anionics, represented in this study by soaps (Table I, Nos. 37, 38) and by dodecylbenzene sulfonate, widely used in detergent formulations (No. 36). Reference to these numbers in Table I shows that none were successful for emulsions of this type.

Nonionic surfactants can be made by reacting ethylene oxide with chemicals having a reactive hydrogen group; e.g., carboxy acid, hydroxyl, amines, or amides.

The general class of nonionics may be divided into several types. Well-known representatives because of wide usage are the Spans, Brij, and Tweens since they were especially designed for emulsion purposes. The Brij materials tested were polyethylene cetyl ethers, varying in polyethylene content (Nos. 5, 35, 47), but none produced satisfactory emulsions. Similar, because it is produced from fatty alcohols condensed with ethylene oxide, is Sterox AJ-100 (No. 7), which also failed to perform satisfactorily.

Another series of ethylene oxide adducts are those comprising alkylphenols. Representatives are Igepal DM 430, Sterox DJ, DF, and JN (Nos. 4, 8, 9, 10), which failed to perform satisfactorily.

Another nonionic variety is that produced by reacting a polyglycol with fatty acids; representative of this are Emerest 2640, 2642, and 2648 (Nos. 17, 18, 19), Myrj 53 (No. 33), and Emulphor ON 870 (No. 29), but none of these proved successful. Yet another type of emulsifier comprising fatty acids reacted with a polyol, or a polyol and ethylene oxide, is represented by Span 40, Tween 20, and Tween 60 (Nos. 6, 41, 43), but here only Span 40, a sorbitan monopalmitate, failed to give satisfactory emulsions.

The amine nonionics were represented by Katapol PN 430, Priminox R-15, T-5, and T-15 (Nos. 28, 30, 31, 32), but none of these performed satisfactorily.

Block polymers of propylene-oxide and -glycol reacted with ethylene oxide, Pluronic L 31, L 62, L 63, and L 101 (Nos. 12, 13, 14, 15) were uniformly unsuccessful. Another kind of nonionic is represented by ethanolamides, but Conco K and DCS (Nos. 24, 25) failed to produce stable emulsions.

Fatty acid amides reacted with ethylene oxide, Ethomids HT/15, HT/60 (Nos. 68, 69) and Cerasynt 303 (No. 1) failed to emulsify the fuel successfully.

In general, then, the only nonionics tested which showed JP-4 emulsifying capability were polyoxyethylene sorbitan-fatty acid products, Tween 20 and 60.

Another class of surfactants tested was the fatty acid amine - lower carboxylic acid salts. Representatives of this class are Armac T and Alamac H26D and 21D (Nos. 2, 22, 23). These agents are mildly cationic (or amphoteric) and are modified by the acetic acid used to neutralize the amine. Most successful of the three was Alamac H26D, which varies from the others undoubtedly by higher molecular weight of the lipophile portion of the molecule. The H apparently signifies hydrogenated; the 26, tallow; and the D, distilled. This compound was one of the most effective emulsifiers tested and proved to be low in ash, making it a prime candidate for the engine combustible formulation.

Amphoteric agents, comprising both anionic and cationic groups in the molecule, represent another surfactant class. Examples of these are Deriphats 151C and 170C (Nos. 20, 21), which are fatty acid amino propionic acids which were unsuccessful; and Armeen SZ and Z (Nos. 55, 63), cocoamino butyrate and crotonate, but only the SZ product showed potential. A coco-hydroxy butyramide (No. 48) failed to produce an emulsion.

Another variety of cationic agent was represented by the amine oxides. Such surfactants are Aromox DMCD and DMHTD (Nos. 56, 57), and Ammonyx SO, LO, and CO (Nos. 58, 59, 60), but none produced satisfactory emulsions.

Another type of bifunctional surfactant is represented by the complex phosphate esters reacted with ethylene oxide, i.e., an anionic-nonionic-type agent. These phosphate esters may be derived from alcohols or alkylphenols, may be mono- or diesters, and may be varied further by the ethylene oxide content. Representatives of this type are Gafac RM 410, Antara LF-200, Emcol CS-141, Antara LE-600, Emcol CS-136, -131, -140, -151, -187 (Nos. 39, 40, 42, 45, 46, 49, 50, 51, 61). These were all received as the free acids; hence, for

use they had to be neutralized, and in this case with an amine-type base.

Free acids may be neutralized with amines with the objective of changing the HLB characteristics of the molecule. Triethanolamine (TEA) provides hydrophilic terminal groups affecting water solubility, while propanol- or butanol-amines comparatively increase lipophile character. To go still further toward the lipophile state, alkylamines of varying alkyl chain length, such as propyl or amyl, may be selected. Highly increased lipophile character may frequently be attained by using di- or polyamines. The built-in lipophile character of the complex phosphate will determine which amine produces the best fuel emulsion. For example, Antara LE-600, Nos. 45-1 through 45-10, shows that less stability occurs by neutralizing with n-propylamine than with TEA. Gafac RM-410 (Nos. 39-1 through 39-4) appears to indicate that either TEA or propylamine may be used, but that the TEA salt gives more viscous emulsions.

The triethanolamine salts of these complex phosphate esters in general proved to be good fuel emulsifiers. Effective emulsifiers were Gafac RM-410, Antara LF-200, Emcol CS-136, Emcol CS-131, and Emcol CS-140 (Nos. 39, 40, 46, 49, 50). Unsatisfactory because of partial loss of stability were Emcol CS-141, Antara LE-600, Emcol CS-151, and Emcol CS-187 (Nos. 42, 45, 51, 61). The Emcol products are portions of homologous series of declared constitution, while the Gafac products were not clearly defined; hence, they were not investigated as fully. The candidate emulsifier selected was Emcol CS-136.

Miscellaneous and other, less important surfactants were explored, but none showed promise.

#### 4. Emulsifier Concentration and External-Phase Variation

##### 4.1 Emulsifier Concentration

A limited investigation was made of the effect of surfactant concentration upon emulsion characteristics. Numbers 24 and 25 (Table I) for Conco K and DCS indicate the results of attempts at increased stability by using larger ratios of surfactant. In neither of these cases did increased surfactant prove useful. Other examples appear for numbers 26 *et seq.* Within the narrow limits available, it appeared that, at best, only slight improvement in stability resulted from this approach.

A series of further experiments was made with the TEA salt of Emcol CS-136 surfactant, where the 3% level of external phase was kept constant and the amount of surfactant was varied. It was found that 0.20% emulsifier met all the requirements of the stability tests; 0.15% emulsifier was stable at -20°F, but broke down after one day at 135°F; and at 0.10% it would not accept all the fuel. These tests are shown in Table I as 62-6, 62-7, and 62-11.

Surfactants "as received" or sold are frequently solutions of the agents, since to prepare them as 100% active agents entails expensive added effort. Surfactants 55 through 60 are of this type, and the -1 emulsions were on the "as received" basis. Since the active ingredient concentrations were 30 to 40%, the 0.3 wt % level was actually reduced to 30% of this level. As a consequence, though these agents showed a degree of effectiveness, they generally failed to perform completely satisfactorily. However, when used on the 100% active ingredient basis, their effectiveness was improved. In general, they failed to perform as satisfactorily as other candidates, undoubtedly due to their structure, though as nearly a homologous series as possible was selected.

#### 4.2 Amine Salts

The complex organic phosphate esters may be used *per se*, but their HLB values can be enhanced by neutralization, in this case preferably with an amine derivative. In most cases the amine salts were postprepared to give neutral salts based upon their neutralization equivalents where these had to be developed, or were prepared on an equimolar basis where the surfactant acid was monoacidic.

Several amine derivatives were used as neutralizers. Because of the multiplicity of ethanol groupings, triethanolamine was the product of choice. Mono- and di-ethanolamine salts are also possible, but their lower hydrophile character indicates that they would be less effective than the tri-salt. Less hydrophile is normal or isopropyl amine of 2-amino-1-butanol (mono-isobutanolamine).

Examples of amine-neutralized compounds are LAS 99 (No. 36) the dodecylbenzene sulfonate, stearic acid (No. 37), oleic acid (No. 38), and others of the complex organic phosphate esters (Nos. 39, 40, 42, 45, 46). Several of the promising surfactants were of this type.

Use of longer chain mono-amines caused lowered water solubility, i.e., lower HLB values; hence, they were not good candidate materials.

Advantages of the amines are their volatility at engine combustion temperatures and their general corrosion-inhibiting character.

#### 4.3 External-Phase Variation

##### 4.3.1 Water-Free Emulsions

Only a single experiment (Table I, No. 41-1) was performed in which ethylene glycol was used alone, dispensing with water entirely. Whereas the water-containing system was reasonably stable, that containing no water was relatively unstable. This approach was to be used only in further attempts to improve stability toward the desired lower temperature value.

Another series of experiments with Emcol CS-136 + TEA was made, where the ratio of components in the water-surfactant phase was kept constant and the percent of the total phase was varied. A 2.5% emulsion met the thermal stability requirements, but a 2.0% emulsion would not accept all the JP-4. A 2.0% emulsion with Antara LE-600 formed, but failed the 7-day 135°F stability test. These tests are 62-8, 62-4, and 62-5, respectively.

The above experiment was repeated with the exception that ethylene glycol in the water phase was substituted with formamide in the Emcol emulsion. External phases of 2.0% and 1.5% met the thermal stability 7-day tests, but no success was obtained in adding excess JP-4 to the 1.5% emulsion. These tests are 62-9, 62-2, and 62-1, respectively.

Experiments also failed when ethylene glycol was substituted for half and then all of the water in the standard 46-1 Emcol CS-136 + TEA emulsion (46-13 and 46-12). The substitution for half of the water succeeded with the Antara LE-600 + TEA emulsion, although there were a few drops of free fuel in the 135°F 7-day test, indicating a borderline case (45-10).

An emulsion preparation was attempted by combining Emcol CS-136 + TEA with Alamac H26D for the purpose of reducing the residue upon burning. While each of these surfactants individually produce stable emulsions, together in equal parts, they were incompatible and did not form a stable emulsion.

##### 4.3.2 Ethylene Glycol Replacements

On the basis that the nonaqueous external-phase constituent should possess several hydroxyl groups, a number of glycol-

like chemicals were secured and tested. The emulsions were prepared with 0.3 wt % Tween 60 and a 3 vol % external-phase ratio. Table I, experiments numbers 44-1 through 44-7, show these data. Test 44-1 shows that glycerine failed to accept all the JP-4, likewise failing with propylene glycol and diethylene glycol (44-2 and -3). No emulsion was formed with dipropylene glycol, Carbowax 300, or methanol (44-4, -5, -6, and -7).

Since hydrogen bonding is a mechanism used to explain the water solubility of most if not all of the nonionic surfactants, substitutes for ethylene glycol with this character were sought. Since amines and amides are of this character, nonionics made from them, and lower chain length materials, should potentially prove to be suitable. Consequently, formamide and acetamide were substituted for ethylene glycol. Complete substitution of these chemicals for ethylene glycol and water was not successful (Nos. 52, 53, 54, Table I) for emulsifiers, as might have been predicted. However, when substituted for ethylene glycol in one surfactant-water composition (Nos. 52-4, 53-3), stable emulsions were obtained at rather low viscosity levels.

While these alkylamides were potential candidates, their relatively high cost as compared with ethylene glycol and their low level of production militated against their usage.

## 5. Variations in Emulsion Technique

### 5.1 Rate of JP-4 Addition

A number of techniques may be used for emulsion preparation. The usual test procedure was to add JP-4 to the external-phase composition slowly, and in portions. Variations were made in this procedure by adding the last, larger portion of fuel in a single quantity once an initial emulsion was formed. Nos. 46-1 through 46-5 of Table I showed that smaller volumes must be added one at a time.

Variations in the technique of fuel addition are described more fully under the Premix section.

### 5.2 Emulsifier Addition

Another common procedure for medium to low internal-phase emulsions is to add the lipophile constituent of a two-part emulsifier to the fuel phase, and the hydrophile portion to the external phase, then combine. Nos. 37-1 and 37-2, and

42-1 and 42-2 indicate that this procedure is not applicable where the external phase is so relatively small.

### 5.3 Premix

The standard method of mixing using the smaller Hobart Kitchen Aid was to start the mixing with the emulsifier and external phase in place and to add the JP-4 slowly over a 10-minute period. This method is satisfactory, though slow, for a mixer such as the Kitchen Aid, which scrapes the bottom of the container. However, for mixers such as the Lightnin' and Dispersator, which incorporate a rotating blade or disc, the 3% of external phase does not provide enough volume for proper mixing action. To overcome this problem, some emulsions were prepared by a "premix" operation, wherein the emulsion was prepared in the Hobart mixer in the standard manner, except that only 10% or 25% of the total fuel was added. This premix was then transferred to the larger volume mixer, and the rest of the fuel was added, this time with sufficient volume for mixing.

Mixing all the components together in one batch and stirring did not form a high internal-phase emulsion. However, it was observed that if the emulsion was at least started at the premix level, then all the remaining fuel could be added at once to form the emulsion. This was done with both the 25% and 10% Emcol CS-136 premix with the Kitchen Aid and Lightnin' mixers. It was also found that the premix could be added to the agitated JP-4 fuel in one batch and still produce a complete emulsion. Advantages to making the premix or one-time fuel addition are in the saving of time and labor and in the bypassing of the chunky or crumbly stage which usually occurred during preparation.

Making the premix with the Kitchen Aid mixer, with its folding-over-type action, caused the incorporation of considerable air and increased the emulsion normal volume by as much as a factor of 4. While the air was found to increase the subsequent rate of emulsification significantly, it also made accurate volumetric metering of the premix difficult, if not impossible. Making the premix at a slow speed with the Lightnin' mixer, when the rotating blade was kept below the surface, produced a satisfactory fluid with very little occluded air.

## 6. Selection of Prime Emulsion Candidates

In the Emulsifier Screening section (3.1), it was shown that nonionic emulsifiers of the fatty acid-ethylene oxide type



provided satisfactory emulsions, as exemplified by Tween 20 and Tween 60 (Nos. 41, 43, Table I). Another type of emulsifier which preliminary screening indicated as potentially satisfactory was that of the fatty acid amine salts of carboxylic acids, such as Armac T and Alamac H26D and 21D (Nos. 2, 22, 23), with H26D appearing to be outstanding.

Another type of emulsifier, a bifunctional type, is represented by complex phosphate esters reacted with ethylene oxide. Examples of these are Gafac RM-410, Antara LF-200, Emcol CS-141, Antara LE-600, Emcol CS-136, -131, -140, -151, and -187 (Nos. 39, 40, 42, 45, 46, 50, 51, 61). These also performed with varying degrees of effectiveness.

These were the only three types of emulsifiers which appeared to provide emulsions of the desired characteristics. To narrow the field, or at least to verify the potential suitability, other tests were selected, and the simplest and most pertinent was determination of compatibility with the mild steel containers used for JP-4 transport.

#### 6.1 Mild Steel Corrosion Tests

Since emulsified fuel is likely to be transported at some time in mild steel drums, and since these are more readily available than lined or coated drums, simple immersion tests were initiated. The effect of the emulsion on steel, and its effect upon emulsion stability, must be recognized. Selected for these tests were the most stable of the emulsions tested.

Pieces of cold-rolled mild steel, 1-in. x 3-in. x 60-mil, were polished with 000 steel wool and emery cloth, and then consecutively rinsed in methanol and pentane to remove all loose particles and oil. A single specimen was then immersed halfway in the various emulsions contained in 4-ounce wide-mouth jars. The results of 7- and 14-day tests are shown in Table III.

The emulsions that caused rusting were in general the hardest to produce and the least stable. Alamac H26D, however, is an exception in that, though it was harder to make, it was stable.

In observing the test emulsions with the steel, it was noticed that the Tween 20 emulsion contained liquid JP-4 after being stored 12 days, and that the Tween 60 and Antara LF-200 emulsions contained free JP-4 after being stored 30 days. Whether the mild steel caused this separation is not known. In all three of the above situations, the separation

TABLE III. 14-DAY MILD STEEL CORROSION TESTS - PARTIAL IMMERSION					
Test Emulsions	Test Period (Days)				
	1	2	5	7	14
JP-4 Fuel	No rust	-	-	-	-
Dist. Water	Heavy rust, above and below waterline, especially at interface				
Tween 20	None	None	Heavy rust on edges*	Heavier	Also on faces
Tween 60	None	Rust on edges and rear interface*	More rust below surface than above	Heavy rust in all areas	-
Alamac H26D	Thin line of rust at interface, some below surface				
Gafac RM 410	None	-	-	-	-
Antara LF-200	None	-	-	-	-
Antara LE-600	None	-	-	-	-
Emcol CS-136	None	-	-	-	-
*Edges were not polished.					
- Indicates no further change.					

was noticed after the completion of the 7-day test. The final results of the test after 30 days are shown in Table IV.

This test showed that the phosphorous-containing emulsions were less corrosive than the straight JP-4 fuel. It also showed that the alkylamide-containing, external-phase emulsions will corrode and that these emulsions break much more readily than the ethylene glycol/water emulsions.

Alamac H26D emulsion caused slight but unobjectionable rusting.

### PART III. PERFORMANCE TESTING

#### 1. Evaluation of Prime Candidates

Based upon the preliminary screening data, two prime candidate emulsions were selected: Emcol CS-136 and Alamac H26D. These were evaluated according to the contract work statement. It was expected that the Emcol emulsion would be the one selected for recovery and that the Alamac would be selected for direct engine consumption, since the latter should be very low in ash and the former should be adaptable to JP-4 recovery by a combination of chemical and mechanical means.

##### 1.1 Thermal Stability

###### 1.1.1 Low-Temperature Stability

Mixtures of ethylene glycol/water have the following normal freezing points: 50/50 at -30°F and 51/49 at -36°F. Decrease in water to a 60/40 level would lower the freezing point still further, to -57°F. Additionally, presence of anti-icing additive (methyl cellosolve) could produce further effect. Emulsifiers also aid in reducing the freezing point, but this effect would probably be marginal. Emulsion stability at low temperatures is obviously important, but the factor of sharply increased yield stress at these levels adversely affects the ability to pump the emulsion to the engine. Table V compares these effects, and indicates that Alamac emulsion is not broken (remains stable) at -40°F, but yield stress is increased almost 10-fold (yield stress values from <1300 dynes/cm<sup>2</sup> at 77°F to 12,100 at -20°F).

TABLE IV. 30-DAY MILD STEEL CORROSION TESTS - PARTIAL IMMERSION AT 75°F

Test Emulsion	Corrosion	Appearance	% JP-4 Separation
JP-4 Fuel	+	General pitted red rust below liquid line.	-
Distilled Water	+	About 1/2-in. layer of loose red rust in bottom of jar.	-
Tween 20	+	Severe red rust below surface, less above.	35
Alamac H26D	---	A few areas of red rust above surface, none below.	0
Gafac RM 410	-	No rust.	0
Antara LF-200	-	No rust, remaining emulsion very thin.	30
Antara LE-600	-	No rust.	0
Tween 60 (Glycol)	++	Severe red rust below surface, less above.	25
Tween 60 (Formamide)	++	Severe black and red rust below and above surface.	50
Tween 60 (Acetamide)	++	Severe black and red rust below surface, less above.	10
Emcol CS-136	-	No rust.	0
Emcol CS-136 (Formamide)	++	Medium mostly black rust on 80% below, 30% above	20
Emcol CS-136 (Formamide, 98.5% Internal Phase)	++	Heavy pitted red rust below and above surface.	100
Emcol CS-136 (Acetamide)	+	Light spotted reddish-black rust on upper part only.	5
- = no change + = mild corrosion ++ = severe corrosion --- = slight corrosion			

TABLE V. THERMAL STABILITY			
Temperature (°F)	Days Storage	Emulsion	
		Alamac	Emcol
-65	7	Unstable	Unstable
-40	7	Stable	Not tested
-20	7	Stable	Stable
135	7	Stable	Stable
160	6	Stable	Not tested
77	30+	Stable	Stable

#### 1.1.2 Freeze-Thaw Stability

Samples of emulsion were cycled from -20° to 77°F for ten periods, assuring that both temperatures were attained before starting another cycle. On some emulsions this type of test is more severe than those at maintained temperatures, but neither the Alamac nor the Emcol emulsion was affected by this treatment.

#### 1.1.3 High-Temperature Stability

As with the low-temperature tests, capped 4-oz bottles of emulsion were stored at the temperatures noted in Table V for a week. Both emulsions were stable at 135°F, and the Alamac was stable for at least 6 days at 160°F.

#### 1.1.4 Room-Temperature Stability

In addition to the thermal stability tests cited above, samples were set aside at 77°F for longer term storage. The emulsions meeting the -20° and 135°F 7-day requirements were stored in glass for their tests. The two main candidates, the Alamac and Emcol emulsions, were completely stable for 30 days, and samples have been stable in excess of 90 days.

#### 1.1.5 Storage Conditions

All the storage tests were made in closed glass containers; where stability was indicated, no separation of JP-4 occurred. However, where storage occurred in open containers at either low- or high-temperature levels, slight separation

of free JP-4 fuel resulted. Two possible explanations for this phenomenon suggest themselves. One is that since the emulsion surface "breathes", i.e., loses fuel vapor to the air regardless of temperature, a degree of syneresis then occurs. The other possibility is that contraction of the external phase occurs upon vaporization, and the separation of fuel then takes place.

In closed containers a degree of the latter mechanism must occur, since a thin film of free fuel was formed, and any further fuel vaporization ordinarily ceased when the air layer above the emulsion became saturated.

## 2. Gravity (g) Loads, Impact and Vibration

The effect of centrifugal action (g loads) on an emulsion can cause emulsion separation, as in cream removal from whole milk. Since these fuel emulsions may be subjected to varying g loads, impact or vibration, tests were made at different g levels and under controlled conditions.

### 2.1 500-g Load

This test was made following ASTM D 96, and was used for screening purposes. Unless an emulsion could meet this requirement (500 g's for 30 minutes), the composition was dropped. The data for this test are given in Table I.

### 2.2 10,000-g Load

In performing the JP-4 recovery tests, a high-velocity DeLaval centrifuge was used, and the Alamac and Emcol emulsions were subjected to this load for 1 minute. Neither emulsion showed any indication of separation.

### 2.3 150-g Impact (Shock)

A shock testing machine constructed in accordance with Specification Jan-5-44 was used to deliver the shock to the specimen. This test was made by Bowser-Morner Testing Laboratories.

A shock spring, of a thickness calculated to produce the specified shock time duration, was designed and fabricated specifically for this test by Bowser-Morner Testing Laboratories, Inc., but spring calibration procedures demonstrated that the flexural strength of the spring exceeded the structural capability of the testing machine carriage, limiting the machine capability to 1-millisecond time duration.

In order to attain 150-g shock in a time duration of 0.00025 to 0.0005 second, it was necessary to design and fabricate a shock spring based on calculations utilizing the following established formulas:

$$T_s = \pi \sqrt{\frac{m}{K}}$$

$$g = \sqrt{\frac{2Kh}{W}}$$

where

- $T_s$  = time, sec
- $m$  = mass of the carriage,  $\frac{\text{lb-sec}^2}{\text{in.}}$
- $K$  = spring constant, lb/in.
- $h$  = height of drop, in.
- $W$  = weight of carriage and specimen, lb
- $g$  = gravity units

Utilizing the above equations, it was determined that a spring having a constant of 1,500,000 lb/in. was needed to provide 1/4 to 1/2-millisecond time duration.

Using this spring constant, the height of drop was determined to be less than 1/8 inch.

Calibration of the spring revealed that the shock machine carriage had a flexural strength of only 300,000 lb/in., which, according to calculations, would provide a 0.001-second time duration. The shock test was conducted as specified, except that 1-millisecond time duration was observed, on a best-effort basis.

The shocked Alamac emulsion showed no difference in appearance from unexposed emulsion. Since this emulsion has withstood g-loads of 10,000 g, the short-duration, comparatively low g exposure would hardly be expected to have any effect.

#### 2.4 Vibration Test

This test was conducted at a vibration level of  $0.4 \pm 0.1$  g according to a specified time-amplitude schedule. The test was performed on 5 pounds of Alamac emulsion in a stainless steel, capped cylinder, 3/4 filled. This test was performed by Bowser-Morner Testing Laboratories, Inc., of Dayton, Ohio.

An MB Model C-10 Type E exciter was used in conjunction with an MB Model T-51-MC Type K control panel to furnish controlled vibratory acceleration to the sample container.

Frequency of applied vibration was regulated by a Hewlett-Packard signal generator, an integral part of the control panel, and was monitored continuously by a Model 5245 Hewlett-Packard electronic counter, S/N 544-08997. Both instruments were calibrated October 18, 1966.

Amplitude of applied vibration was monitored continuously by an MB Model M3 vibration meter, S/N 1153, which was calibrated October 18, 1966, and was verified periodically with a calibrated Bausch and Lomb optical instrument, readable to the nearest 0.05 millimeter.

Time of sustained vibration at specified frequencies was regulated with a laboratory-type stopwatch.

The sample container was adapted to a vibration exciter and subjected to 24 continuous hours of vibration at 0.4-g acceleration and at time durations and frequencies as follows:

<u>Vibration Time, hr</u>	<u>Frequency, cps</u>
1	5.0
1	32.0
2	5.9
2	7.0
2	8.25
2	9.75
2	10.9
2	13.75
2	16.2
2	19.2
2	22.6
2	27.0
2	32.0

These times and frequencies were specified in contract modification Number 1.



The Alamac emulsion sample yield values before and after vibration were:

	Yield Values (dynes/cm <sup>2</sup> )
Before	1170
After	1200

There was no separation of JP-4, and the emulsion appeared to be quite normal.

### 2.5 "Slosh" Test

The emulsions were given a 24-hour room-temperature shaking test. Eight-ounce wide-mouth jars were half-filled with emulsion and mounted on a shaker having a horizontal travel of 1-1/2 inches at the rate of 240 cycles a minute.

The vibration or sloshing caused no breakdown of the emulsions and, in fact, made them thicker than they were at static conditions, possibly due to air incorporation.

### 2.6 Discussion

The foregoing data, summarized in Table VI, show that acceleration of gravity, slosh, impact, and vibration are unlikely to affect adversely the stability of these emulsions. However, because of peculiar operating conditions set up in aircraft, partially filled containers should be subjected to actual flight conditions in aircraft in which emulsion might be used, for at least the time for a single mission, preferably longer.

TABLE VI. GRAVITY (g) LOAD, IMPACT, "SLOSH," AND VIBRATION TESTS (Conditions noted under 2.6 - Discussion)			
Test	Time	Stability	
		Alamac	Emcol
500 g	30 minutes	stable	stable
10,000 g	1 minute	stable	stable
150-g Impact	1 millisecond	stable	stable
"Slosh"	24 hours	stable	stable
Vibration	24 hours	stable	stable

### 3. Flow Properties

The desired flow properties of these emulsions were defined such that the emulsions would resist flow out of a hole in a tank wall similar to a projectile puncture, yet would be capable of being pumped through conventional aircraft plumbing. The following data show the laboratory progress through simulation of the projectile hole requirements, i.e., 1/2-inch diameter by 2-inch length, through process control measurement methods, to a more effective and definitive flow property measurement.

#### 3.1 Projectile Hole Simulation Rig

To perform this test, a simple rig was devised consisting of a copper tube, 2-3/32 inches in diameter by 10 inches in length, capped at the lower end, and fitted at the upper with a cap and a pressure gage at a T to permit pressurization.

The tube was filled to a 6-inch level with a Tween 60 emulsion (No. 43-1), after applying a rubber stopper to the 2-inch length of outlet tube 1/2-inch inside diameter. Upon removal of the stopper, about 1/4 of the emulsion ran out quickly, more issuing as small chunks. For the remaining 2/3 of the emulsion, not then issuing, a 1/4-pound nitrogen pressure was applied, and the rest of the emulsion flowed quickly from the exit tube.

In another experiment, an emulsion with Antara LF-600-TEA salt (No. 45-3, Table I) was added to the rig to give a 6-inch fluid head, without any gravity flow. About 10% flowed out with 1/2-pound pressure.

#### 3.2 Brookfield Viscometer Method

Since the flow characteristics of the emulsions were defined by the simulation jig, a quantitative measure of viscosity was desired, and the relatively effective, easily applied Brookfield Viscometer was investigated. The RFV model was used for these tests.

This method appeared to provide satisfactory control values with a minimum expenditure of time. While not the most ideal for these types of compositions, the data nevertheless were considered a valid indication of comparable consistencies and tendency toward thixotropy. Examples of this phenomenon are apparent from Table I. These data were useful for screening purposes, permitting selection of compositions falling in the desired apparent viscosity range.

Correlating the Hole Simulation Rig with the Brookfield values showed that the Tween 60 emulsion at 60,000 cps would flow relatively easily, but that 1/4- to 1/2-pound pressure was needed to cause the Antara LE-600-TEA composition to extrude (this emulsion has an apparent viscosity of 230,000 cps).

The candidate surfactant emulsions all fell within a 50,000- to 170,000-cps range. The fact that different batches (e.g., 45-2 and 45-3) varied in viscosity indicated that the method of preparation or the age of emulsion might rather strongly affect ultimate results. It appeared that total emulsion age affected final viscosity (i.e., measured after 30 days at 77°F). Data of Table I show that aging effects were variable, and depended upon the emulsifier. Sample No. 40-1, Antara LF-200-TEA salt, had a viscosity of 90,000 cps at once, and 80,000 cps after aging a week. Another example, Tween 60 (No. 43-3), was 30,000 cps at once, 60,000 cps after one week, then 10,000-20,000 cps after three weeks.

Since the Brookfield data vary, depending upon the spindle used and the thixotropy of the emulsion, a more definitive method was indicated. One, the falling ball method, could be used for quality control during production. Since the falling ball values are not as precise as desired, an extrusion rheometer using the Instron was also tested. However, it failed to provide satisfactory data. The experiments with these two viscometers are cited in Appendix III.

Another approach to the viscosity measurement problem was the use of a grease penetrometer.

### 3.3 Penetrometer Yield Point

A standard Cone Penetrometer which conforms to ASTM D 217-65T specification was used in this work. Since the standard 150-gram cone assembly made of brass and steel was too heavy for our work, a 49.5-gram cone assembly with identical dimensions was machined out of polypropylene (large cone) and aluminum (small cone and shaft).

Ordinarily, a metal shaft, with a knurled wheel located at its center, screws into the shaft of the cone assembly and stops the cone from completely falling out of its holder. Because of the "thinness" of our emulsions, it failed to give a reading with this "limiting" knurled screw in place. Therefore, the screw was removed for our determinations.

With the knurled screw in place and the cone assembly pushed up as far as it would go, the penetrometer read zero. With the knurled screw removed and the cone assembly pushed up as far as it would go, the penetrometer read -0.13 cm. Therefore, this value must be added to the actual penetrometer reading for final calculations.

Procedure - A liter beaker is filled above capacity with emulsion, and the top is then leveled with a straightedge. The knurled screw is removed from the penetrometer, and the cone assembly is pushed up as far as it will go. The cone is adjusted so that the tip just touches the emulsion surface and is then released for 5 seconds. The knurled screw is replaced, and the depth of penetration is read on the instrument. 0.13 cm is added, and this value is called P in the following calculation.

Calculation

$$\text{Weight of Cone} = 49.5 \text{ grams} = 48,500 \text{ dynes} = f_1$$

$$\text{Surface Area-Aluminum Cone} = 2.4 \text{ cm}^2 = f_2$$

(with a depth of 1.6 cm)

Surface Area-Plastic Cone Frustum as a Function of Depth of Penetration, P(in cm)

$$4.34[0.95(P-1.6)+0.94][P-1.60] \text{ as cm}^2 = f_3$$

$$\text{Yield Point (supporting strength)} = \frac{f_1}{f_2 + f_3}$$

$$48,500 \text{ dynes} / (2.4 \text{ cm} + f_3)$$

Figure 1 presents yield stress vs penetration values for rapid conversion. NOTE: This analysis does not account for buoyancy effects.

This method was used in measuring the various batches of large-scale production lots. The following table shows a comparison of the Brookfield apparent viscosity and penetrometer yield values, and is typical for the preferred emulsions:

TABLE VII. FLOW PROPERTIES (77°F)			
Apparent Viscosity (cps)		Yield Value (dynes/cm <sup>2</sup> )	
		At Once	Several Days
Alamac	90M	2100	1400
Emcol	90-100M	3400	2300

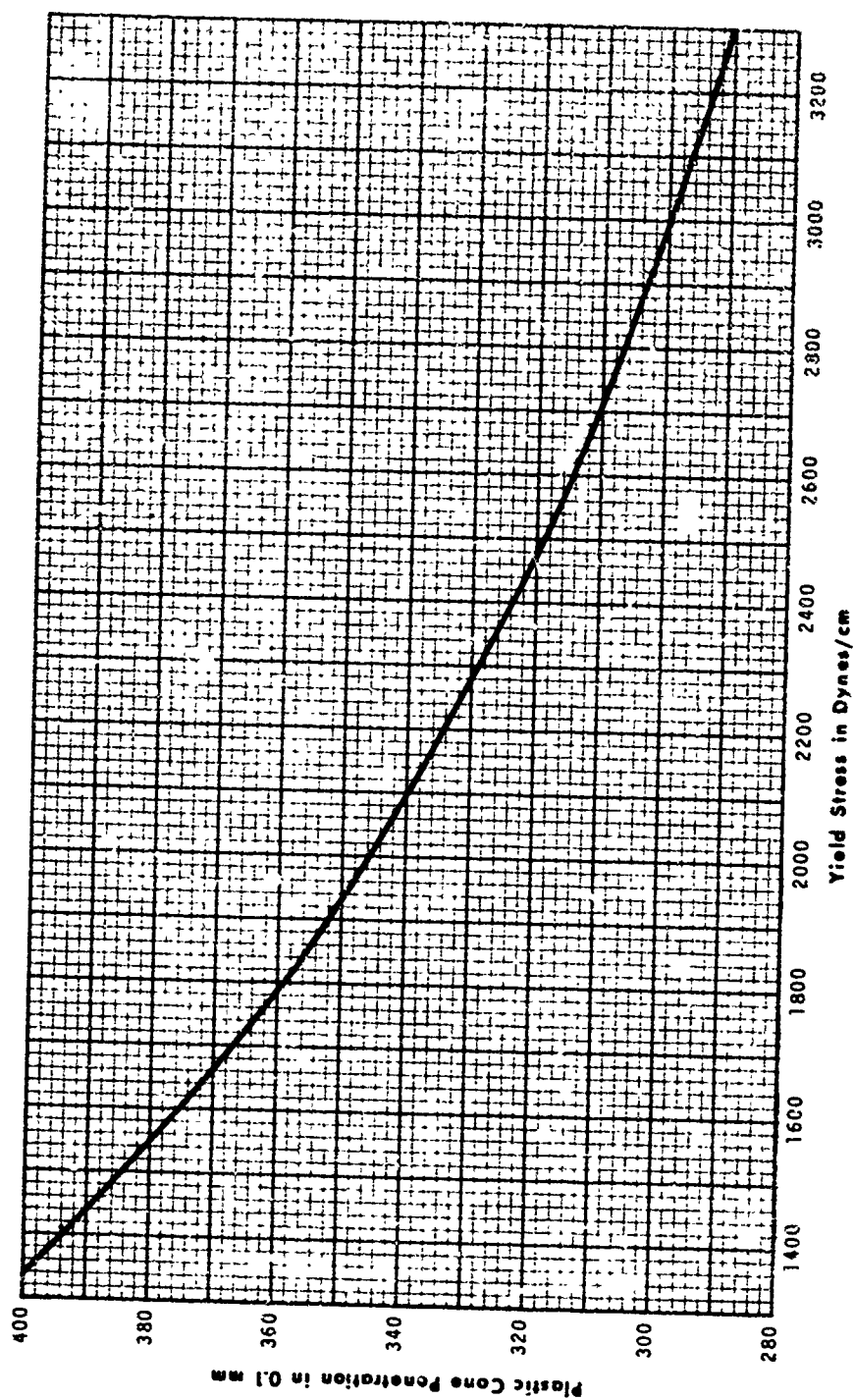


Figure 1. Penetration vs Yield Stress.

### 3.4 Yield Stress Variation With Age

It has been observed that though emulsions are very viscous immediately after preparation, they become more fluid upon standing. This was demonstrated when the yield stress was determined on composite samples when they were 1, 2, 5, 6, and 7 days old. Originally they measured about 2800 dynes/cm<sup>2</sup>.

TABLE VIII. YIELD STRESS VARIATION WITH AGE			
Sample	Age (Days)	Yield Stress	Density (grams/cc)
#1 Composite	7	1360	0.727
#2	6	1480	
#3	5	1700	
#4	2	1760	
#5	1	1980	0.724

The results show that the greatest change in viscosity occurred the first day. The almost negligible difference in density indicates that the reason for viscosity change is a rearrangement of external phase rather than loss of entrapped air. These density values appear to be consistent though low.

### 3.5 Low-Temperature Yield Stress

A 1-liter beaker was filled with Alamac emulsion and leveled flat with a straightedge. The beaker was covered with aluminum foil to prevent evaporation, and was stored with the cone assembly of the penetrometer in a cabinet at -20°F. Sixteen hours later they were removed, and a penetration reading was quickly taken. A yield stress of 12,100 dynes/cm<sup>2</sup> resulted.

The emulsion was very stiff at this temperature and had no resilience when a rod was plunged into it.

#### 4. Vapor Properties

##### 4.1 Rate of Evaporation

Evaporation tests of the emulsions measure the supply of volatile fuel to the air space above the emulsion, with negligible loss of external phase. What may be visualized is the collapse of individual emulsion droplets with loss of volatile fuel, withdrawal of the collapsed external phase, followed by replacement by droplets of fresh emulsion. The replacement phenomenon is understood when it is realized that emulsion systems are dynamic and in motion and not necessarily static. In a closed system, the air above the emulsion will reach an equilibrium content of vaporized JP-4 essentially identical with that of closed JP-4 systems (see Emulsion Vapor Pressure). It is not this static, equilibrium condition with which the current tests are concerned. The objective is to determine the amount of JP-4 lost in an open system, as a function of time and temperature.

The procedure used in these tests was as follows:

A 3.8-inch-diameter Petri dish 1/2 inch in height was filled with emulsion and the surface leveled with a straightedge. In the  $77^{\circ} \pm 2^{\circ}\text{F}$  and  $-20^{\circ} \pm 2^{\circ}\text{F}$  tests (in a Sub-Zero cabinet), the dish was placed on a torsion balance, and the weight was measured at once and after every hour for a total of 6 hours. For the  $135^{\circ} \pm 5^{\circ}\text{F}$  temperature, the dish was weighed at once, transferred to a thermoregulated hot plate, weighed hourly by transfer to the balance, and returned to the hot plate in a vented hood. The percentage weight loss was then plotted as a function of time.

As could be expected, the evaporation rate at  $-20^{\circ}\text{F}$  was quite low, but as Figure 2 shows, even after 6 hours JP-4 loses 10%, while the loss is slightly less than 2% for the Alamac emulsion, a factor of 1:5. The Emcol emulsion lost about 0.25%, suggesting that at this temperature the normal vapor pressure is low, or that as a semisolid, loss of fuel from the surface was prevented.

Figure 3, for  $77^{\circ}\text{F}$ , shows that the emulsions were essentially identical in vapor loss and evaporated at a ratio of about 1:9 vs JP-4 after 6 hours.

Figure 4 shows that the emulsions were closely alike at  $135^{\circ}\text{F}$  and that the evaporation rate vs JP-4 was about 1:8. The large change came within the first hour, with loss of the highly volatile low ends; here the ratio was 1:9.

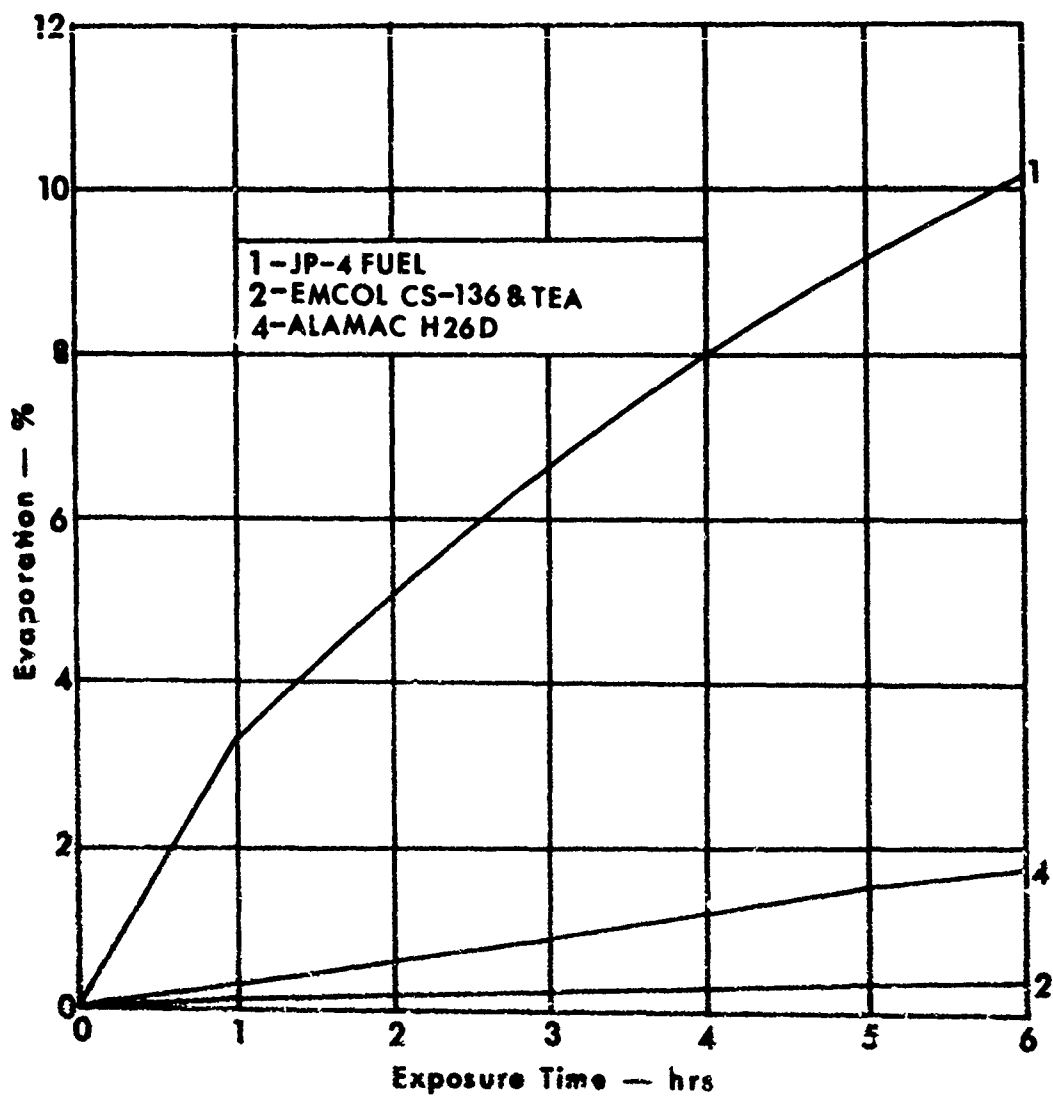


Figure 2. Evaporation Rate at -20°F From 1/2-Inch-Deep Petri Dish in a Sub-Zero Cabinet.



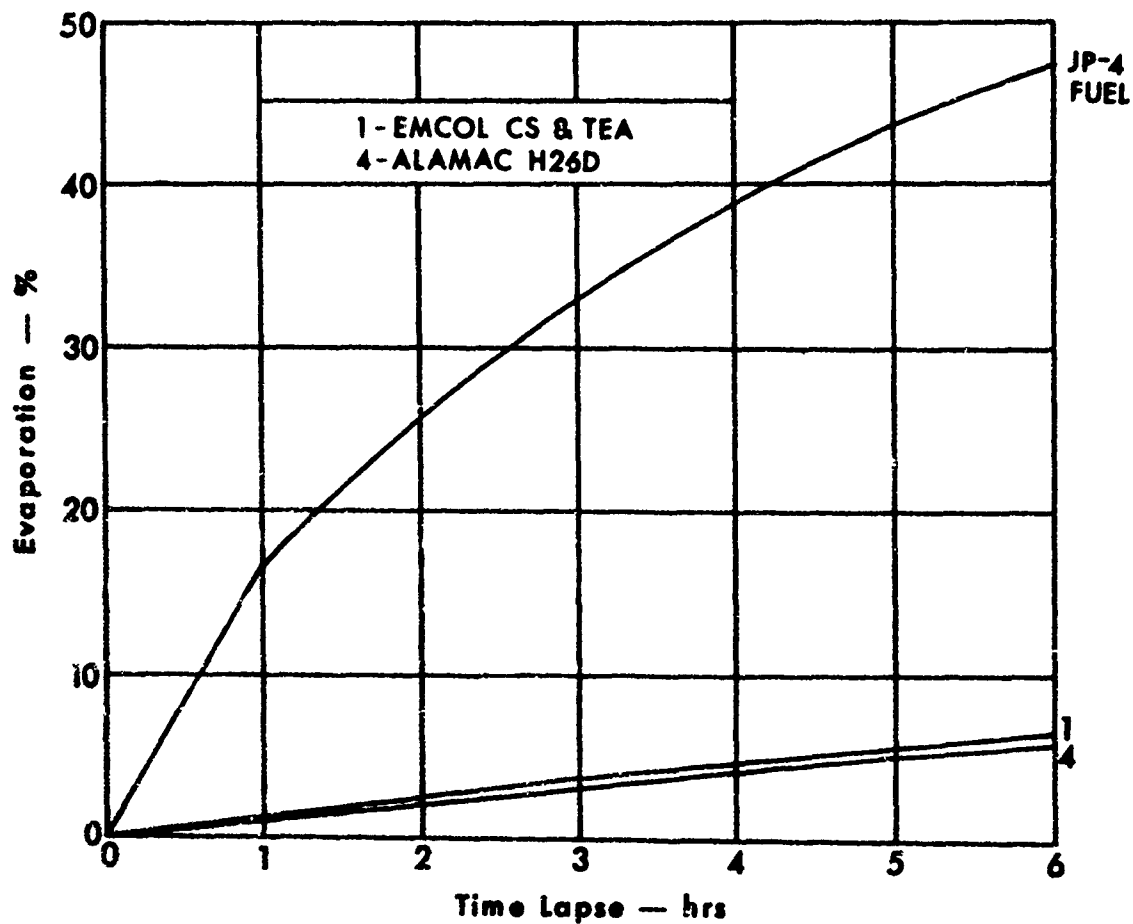


Figure 3. Evaporation Rate at 77°F From 1/2-Inch-Deep Petri Dish in a Sub-Zero Cabinet.

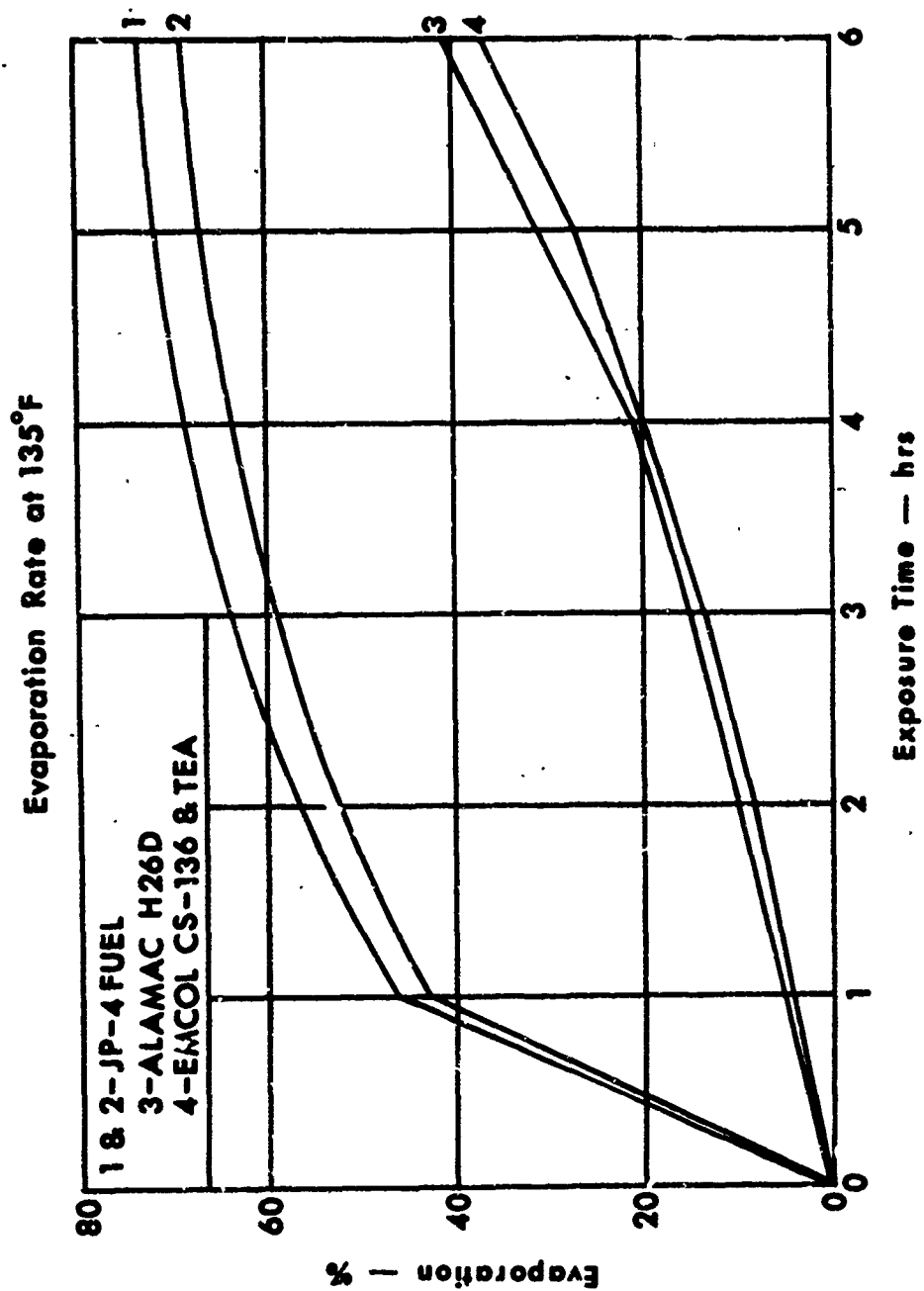


Figure 4. Evaporation Rate of JP-4 Fuel Emulsions at 135°F From 1/2-Inch-Deep Petri Dishes on a Hot Plate in a Vented Hood.

#### 4.2 Emulsion Vapor Pressure

The vapor pressure of Alamac emulsion was determined by the Reid vapor pressure method at 100°F. Shown in Table IX are the vapor pressures of the original JP-4, of the emulsion, and of JP-4 recovered from the emulsion.

TABLE IX. EMULSION VAPOR PRESSURE	
	Reid Vapor Pressure (psi)
Original JP-4	3.15
Recovered JP-4	2.53
Alamac Emulsion	2.55

At equilibrium it might be expected that the vapor pressure of the fuel and the emulsion would be the same, and indeed this was the case. The difference between the value for the original fuel and that for the emulsion or recovered fuel is attributed to the loss of highly volatile low ends and reflects the result of exposure during handling.

#### 4.3 Effect of Shear on Evaporation Rate

The rate of evaporation of most liquids will vary according to the amount of surface area exposed and the vertical movement of liquid which continually brings fresh fluid to the surface. While uniform stirring of a common fluid such as JP-4 will give reproducible evaporation rates at set conditions, this is not so with the viscous Alamac emulsion, which will not even level itself in a container.

A calibrated beaker of emulsion was connected to the inlet of a gear pump, and the emulsion was recirculated from the bottom of the beaker back into the top. The evaporation loss was measured volumetrically. This test was performed using a calibrated stainless steel beaker and a 1700-rpm gear pump. Twenty-four hundred milliliters of emulsion filled a depth of 7-1/2 inches with a surface area diameter of 5 inches. The gear pump produced an intermittent flow of 120 ml/min, because the 1/4-inch tube inlet of the pump acted as a restriction. Five hours of recirculation caused exactly 100 ml of emulsion to evaporate, equivalent to 4.2 vol %.

## 5. Flammability

The relative flammability of these emulsions can be determined in several ways. Since JP-4 vapors are easily ignited, the relative rates of vaporization represent one approach. Potential explosivity of the vapors is still another. Flash points are also indicative. The time required for an emulsion to begin to burn under certain conditions represents a still further approach. The characteristics of burning JP-4 or emulsion are important to understanding the rate of flame propagation, as is the type of flash occurring upon impact. Each of these tests provides valuable information regarding the flammability of these materials.

### 5.1 Flash Points

The flammability points of the three emulsions were determined via the Cleveland Open Cup Test Method of ASTM D 92-57. A 3/16-inch-diameter flame was passed directly over the emulsion cup after every 5°F increase. The surface of the emulsion was kept 7/16 inch from the top of the cup, and the emulsion was heated at the rate of 5°F per minute. The times and temperatures at which the various emulsions ignited in ambient air are shown in Table X.

TABLE X. CLEVELAND OPEN CUP FLAMMABILITY POINTS		
Emulsion	Ignition Time Lapse (Min)	Flash Point Ignition Temperature (°F)
Emcol CS-136	17	155
"	18	155
Antara LE-600	16	150
"	20	155
Alamac H26D	15	135
"	16	140
JP-4 Fuel	0	77
"	0	77

## 5.2 Ignition Time Lapse

This test was run with the Cleveland Open Cup apparatus, where the flame was kept continually over the emulsifier cup until the emulsion ignited. Whereas the JP-4 caught fire almost immediately, none of the three emulsions in Table X ignited after a 1-hour exposure at 75°F.

## 5.3 Emulsion Burning Rate

Emulsions in 15.0-gram quantities were weighed into aluminum weighing dishes 2-1/4 inches in diameter. This preliminary work was done in a hood, and the burning period was measured from ignition to extinguishment.

The following data were obtained:

TABLE XI. EMULSION BURNING RATE	
Surfactant	Burning Time
JP-4 Fuel	6'02", 6'34", 5'43"
Emcol CS-136	6'05", 6'23"
Tween 60	6'20"
Antara LE-600 (0.4%)	6'28"
Antara LE-600 (0.3%)	6'36"

The emulsions started to burn at a slower rate than did straight JP-4 fuel. However, after a few seconds, the heat from the flame began breaking down the emulsion until the entire emulsion was as liquid as JP-4 (usually within a minute). After the initial few seconds, the emulsion appeared to burn with the same intensity as the JP-4 fuel. Most of the burning "liquefied" emulsions spat tiny fireballs, probably from the released external phase.

## 5.4 Explosivity Tests via Mine Safety Appliances Explosimeter

A 3.8-inch-diameter Petri dish (1/2-inch-deep) was level-filled with emulsion and placed in the bottom of a 5-gallon glass jar. The sampling line of the M.S.A. Model 40 Explosimeter was then inserted through a hole in the lid so that its end was in the center of the jar. Every 5 minutes (for a total of 100) the atmosphere at that point was sampled,

and the percentage of the lower explosive limit (LEL) of JP-4 in air at 0.5% was read on the indicating dial.

The results are shown in Figure 5. While the LEL of the straight JP-4 fuel was reached in 24 minutes, only between 40% and 75% of the LEL was reached after 100 minutes with the JP-4 emulsions.

Ultimately an equilibrium condition for the emulsion would be achieved, but this test shows the sharp reduction in this value, indicating a greater safety factor in emulsion usage.

### 5.5 Flame Propagation

A 10-ft trough of 1-1/2-in. angle iron was filled with either JP-4 or Alamac emulsion, which was then ignited at one end. The time required for the flame to propagate the length of the trough was measured with a stopwatch. The same experiments were repeated with a 2-inch barrier (1-1/2 in. high) at the middle of the trough. The results are shown in Table XII.

TABLE XII. FLAME PROPAGATION-BARRIER			
Fuel	Condition	Trough Length	Time, sec
JP-4	No barrier	10'	2
JP-4	2" barrier	5'	2
Alamac	No barrier	10'	107
Alamac	2" barrier	5'	227

All tests were performed in a building free of drafts at 76°F.

Additional tests of flame propagation along the 10-ft trough were run with JP-4 and Alamac emulsion.

When emulsion was burned, the trough was filled to capacity (ca. 2 qts), and the top was leveled with a straightedge. When JP-4 was burned, the trough was filled so that the level was about 1/16 in. from the top, thus allowing only a small volume to boil over the sides.

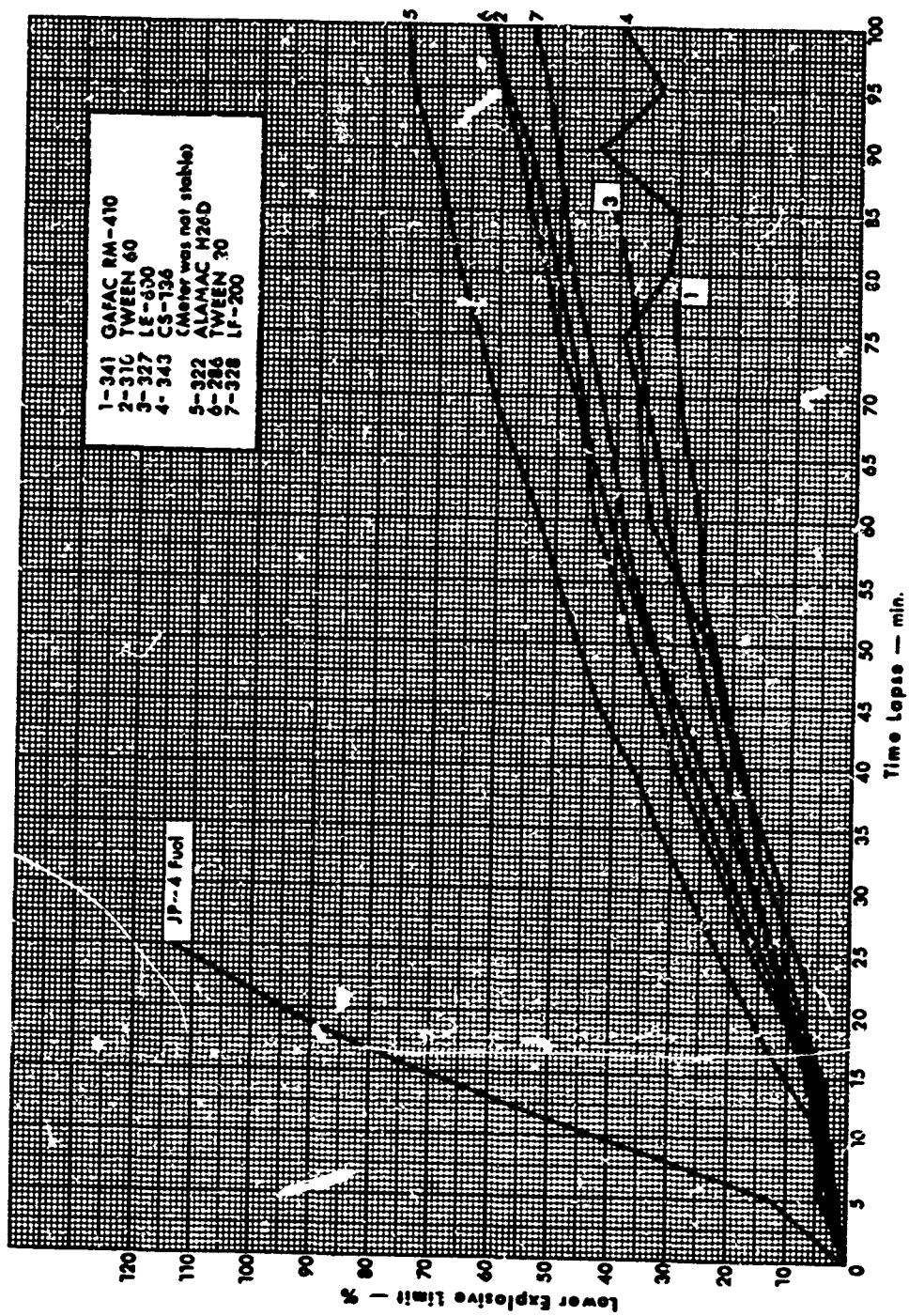


Figure 5. Percent of Lower Explosive Limit (0.6%) of JP-4 Fuel.

Flame propagation times were measured twice for both JP-4 and emulsion, and movies were taken of each experiment. The results are listed in Table XIII. A picture of the emulsion burning is shown in Figure 6.

TABLE XIII. FLAME PROPAGATION TESTS	
Fluid	Propagation Time (sec/10 ft)
Alamac Emulsion	160
"	190
JP-4	2
"	2

#### 5.6 Dynamic Burning Studies

Dynamic burning tests were performed on JP-4 fuel and the Alamac H26D fuel emulsion in order to determine to what extent emulsification of the fuel prevents formation of an ignitable mixture on impact. For these studies, thin-walled metal containers filled with the test media were impacted on a steel screen. The containers were designed to burst on impact and to spray the fuel through to a flame directly behind the screen.

The projectiles were fired from a 37-mm gas riot gun using 1.002 grams of FFg black powder and newspaper wadding. The gun, a 37-mm cartridge, and a projectile are shown in Figure 7. The aluminum tubes measured 1-1/2 in. in diameter by 6 in. long and had a 0.055-in. wall thickness. Aluminum weighing dishes were formed over the ends and sealed with epoxy adhesive after the tubes were partially filled with the fuel to be tested. Equal volumes of JP-4 fuel and the emulsion were tested (79 ml), resulting in total projectile weights of 70 to 80 grams, respectively. The target consisted of a 12-in. x 12-in. steel screen with a 1-in. grid. A propane-air flame burned directly behind the screen (see Figure 8). The gun was fired from a distance of 25 ft, and high-speed motion pictures were taken to measure both the projectile velocity at impact and the size of the resultant fireball.





Figure 6. Flame Propagation of Alamac Emulsion.

37-mm Gas Riot Gun      Projectile      37-mm Cartridge

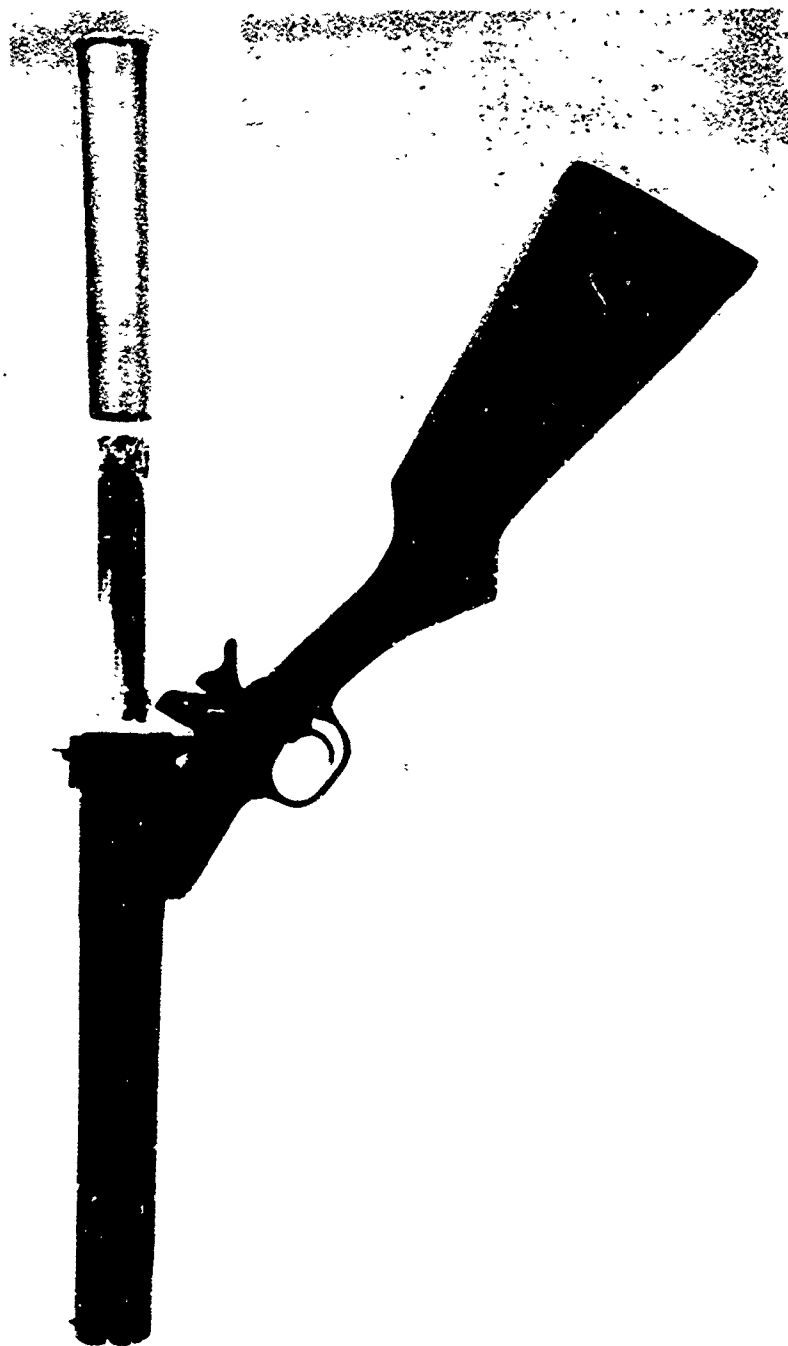


Figure 7. Dynamic Burning Test Gun, Projectile, and Cartridge.  
(37-mm gas riot gun, projectile containing fuel, and  
37-mm cartridge assembly used in dynamic burning  
studies of JP-4 fuel and Alamac H26B fuel emulsion.)



Figure 8. Dynamic Burning Test Grid and Flame.

A summary of resulting data is presented in Table XIV. Nine firings were made of both the JP-4 fuel and the Alamac H26D emulsion. Generally, the emulsion produced a significantly smaller fireball than did the JP-4 fuel. Comparison of the average fireball sizes shows that the emulsion yielded a fireball only 17% as large in cross sectional area as did the JP-4 fuel (i.e., areas of 6.6 and 38.4 ft<sup>2</sup>). The only inconsistent data point (6-ft diameter) for the emulsion was attributed to a high-angle impact of the projectile with the screen. An impact with the projectile axis parallel to the screen yielded the most uniformly shaped fireball and reproducible results. In addition to producing the smallest fireball, in certain instances portions of the emulsion contained in the projectile were able to pass through the flame unburned.

TABLE XIV. SUMMARY OF DYNAMIC BURNING STUDIES		
Approximate Fireball Diameter (ft)		
	JP-4 Fuel	Alamac H26D Fuel Emulsion
	6	2
	5	3
	7	3
	6	2.5
	8	2.5
	7	2
	8	6
	9	3
	<u>9</u>	<u>3</u>
Average	7.2	2.9
Average Fireball Cross Sectional Area	= 38.4 ft <sup>2</sup>	6.6 ft <sup>2</sup>

It can thus be concluded that emulsification of JP-4 fuel results in a very significant decrease in the amount of ignitable mixture produced by a high-velocity impact.

#### 6. Btu's per Pound of Emulsion

The substitution of 3 vol % external phase for JP-4 would be expected to reduce the heat of combustion of the emulsion. This was determined according to ASTM D 240.

TABLE XV. HEAT OF COMBUSTION DATA				
Sample	Gross Heat of Combustion, Btu/lb	Average Btu/lb	% H*	Net Heat of Combustion, Btu/lb
JP-4	20,194	20,141	14.60	18,809
	20,113			
	20,116			
Alamac H26D	19,411 19,442	19,426	14.42	18,130
Emcol CS-136	19,486 19,422	19,454	14.41	18,159
*Galbraith Laboratories, Inc.				

The heat of combustion was reduced about 3.5%, about equal to the 4.1 wt % external phase.

Procedure - Net heat of combustion was calculated using

$$\Delta H_c \text{ net} = \Delta H_c \text{ gross} - 91.23 \times \% H$$

and was corrected for heat liberated when water vapor condenses to water (liquid) in the bomb. This is useful heat and is more nearly representative of conditions of use. Because the emulsions contain 1.80 wt % water, which will yield zero gross heat, a correction must be applied to the percent hydrogen found in the emulsions. The hydrogen due to the water must be subtracted.

### Hydrogen in Emulsions

Fuel	14.6 % H	x 0.957	= 13.97
Water	11.2 % H	x 0.0184	= 0.21
Glycol	9.74% H	x 0.02	= 0.02
Emulsifier	10.0 %	x 0.004	= 0.04
14.24% H expected for emulsions			
(Found: 14.42% and 14.41%)			

The correction, then, for an emulsion of the above composition is 0.21%. This factor should be subtracted from the percent H analyses for the emulsions.

The heat of combustion was derived on a calculated basis as follows. The composition - 776 ml of fuel, 11 ml of water, 11 ml of glycol, and 2.4 grams of emulsifier (Alamac H26D) - was the following:

			<u>Wt % Comp.</u>
Fuel	776 x 0.7526	g/ml = 584.02	95.79
Water	11 x 1	g/ml = 11	1.80
Glycol	11 x 1.1155	g/ml = 12.27	2.01
Emulsifier	2.4 x 1	g/ml = 2.4	0.39
		609.69	99.99%

Multiplying the gross heat of combustion of each component of the emulsion by the %/100 of its composition and summarizing the results should yield a value close to the experimental value for the gross heat of combustion of the emulsion:

Fuel	20,141	x 0.9579	= 19,293
Water	0		= 0
Glycol	8,250	x 0.0201	= 166
Emulsifier	10,000*	x 0.0039	= 39
			19,498 Btu/lb

\*Estimated

This is fairly good agreement with the values found: 19,426 and 19,454.

### 7. Emulsion Ashing Tests

If emulsions are to be consumed directly in the engine, a minimum of residue as ash should be formed. Straight nonionic surfactants will be completely consumed, but surfactants

containing phosphorus in the molecule may result in residual ash. To determine the validity of this approach, one of the phosphorus-containing complex acid salts, Antara LE-600-TEA, No. 45-3, was ashed. For comparison purposes, a similar test was made with straight JP-4. About 12 grams (accurately weighed) of fuel or emulsion were weighed into tared crucibles, burned off at ambient conditions, then fired at 1600°F to complete the combustion. JP-4 had an ash content of 0.052%; the emulsion, 0.070%. This appeared to indicate that a small increase in ash resulted from the use of 0.3% surfactant on the finished emulsion basis.

In a further test, since engine combustion temperatures are in the 3000°F range, preliminary ashing tests were made at 2600°F, the muffle capacity. However, no suitable crucible was found that would retain constant weight at that temperature. Platinum lost considerable weight and its crystalline structure began to deteriorate. Graphite, nickel, and silicate crucibles are advertised for use as high as about 2100°F. Due to this difficulty, ashing determinations were again made at 1600°F in an oxidizing atmosphere. Over 200 grams of each fuel were evaporated to dryness on a hot plate and then placed in a 1600°F muffle furnace for one hour. The percent of ash remaining in each case was as follows:

<u>Fuel</u>	<u>% Ash</u>
Straight JP-4	0.000
Alamac H26D	0.002
Emcol CS-136	0.016
Antara LE-600	0.027

Note: Each emulsion was tested in triplicate.

The high ash content of the Emcol and Antara emulsions is probably due to nonvolatile and incombustible phosphorus in the surfactants. The neutral pH of the ash, however, indicates that if the ash contains phosphorus, it is in a water-insoluble state.

Further, more pertinent data on ash are given in the section on JP-4 Recovery.

## 8. Compatibility Tests

### 8.1 T63 Fuel Pump and Control Seals

O-rings, diaphragms, and gaskets from Bendix and Pesco were submitted by Allison Division for testing with emulsified fuels. Since the number of materials received was small, the Alamac H26D and Emcol CS-136 emulsions were chosen and tests were limited to hardness, weight change, and volume change. Since these tests were made on single samples, the data are no more than indicative.

Each seal was weighed in water and air and the Durometer hardness was measured (ASTM D 676). The seals were immersed in the respective emulsions and stored at 135°F for 7 days. They were cooled overnight to room temperature, and ASTM D 471 test procedure was followed for cleaning and weighing the specimens in air and water. After sitting in ambient air overnight, the hardness was again measured and the change was noted. The results of the above tests are shown in Table XVI.

As a result of the immersion test, some of the emulsion was broken down into free JP-4. The amount of fuel separated in comparison to size of the test specimen was noted, and each specimen was given a relative rating regarding emulsion deterioration. This rating is tabulated in Table XVI.

It should be noted that the emulsions deteriorated from contact with a relatively large seal exposure area and over a period of time much longer than actual use conditions.

### 8.2 Allison T63 Bench Tests of Model 250 Fuel System Components

A summary of the Allison findings follows. The entire report is included as Appendix VII.

The fuel system components tolerated the emulsified fuel quite well, with only the fuel pump filter element showing a slight evidence of corrosion. Several other parts were discolored, but this was not thought to be detrimental.

The individual components retained their original calibrations after the emulsified fuel test.

Control metered flows were less with the emulsion than with the liquid fuel.



TABLE XVI. COMPATIBILITY OF ELASTOMER SEALS WITH JP-4 EMULSIONS									
Material	Durometer		% Weight Change		% Volume Change		Emulsion Breakdown; Color Extraction		
	Emcol CS-136	Alamac H26D	Emcol CS-136	Alamac H26D	Emcol CS-136	Alamac H26D	Emcol CS-136	Alamac H26D	Alamac H26D
Buna S	-2	-6	+24	+30	42	59	small; none	large; none	
Buna N	+3	+1	34	34	55	49	small; none	large; none	
Buna H	0	+1	30	35	49	55	medium; none	large; none	
Paracrill 18-80*									
Diaphragm 343451	-4	-2							
Belloves	0	0	12	14	20	21	medium; none	large; pink	
Rim	-3	-2	25	29	42	47	small; none	large; yellow	
O-Ring 557-S-6	-6	-6	70	55	91	68	none; none	small; none	
Gasket 343489	0	0	16	22	22	25	medium; none	very large; yellow	
Diaphragm 02-12904	0	0	18	18	24	30	medium; pink	very large; pink	
O-Ring MS-29512-6	-5	-5	17	18	28	29	large; pink-yellow	very large; yellow	
O-Ring MS-29512-8	-6	-5	21	23	35	38	large; pink	large; none	
O-Ring MS-29512-3	-3	-2	20	24	35	40	medium; pink	large; none	
O-Ring MS-29513-19	+1	-1	19	21	32	41	large; pink	large; yellow	
O-Ring MS-29513-014	+2	+2	12	19	24	30	small; yellow	medium; yellow	
O-Ring MS-29513-010	+2	+1	12	17	25	27	medium; yellow	medium; yellow	
O-Ring MS-29513-013	+1	+1	12	21	23	34	medium; yellow	large; yellow	
*Butadiene-acrylonitrile copolymer									
**MIL-P-5315 (Buna N)									
***MIL-P-5315 Parco 457-60									

Fuel pump filter pressure drops ran considerably higher with the emulsion, resulting in bypassing action.

An estimated breakdown of the emulsion of 10% to 20% into liquid JP-4 at the control outlet was noted.

The nozzle spray cone closely resembled that of JP-4, but the spray angles were greater while flowing the emulsion up to 250 psi, then lower through about 500 psi.

### 8.3 Coatings

A polyurethane integral wing tank coating (MIL-C-27725) and Buna N repair coating (MIL-S-4383) were applied to aluminum panels according to directions, and in one set the polyurethane coating was further coated with Buna N. The data of Table XVII show that the emulsion attacks the Buna N repair coating and slightly softens the polyurethane coating under the test conditions, which are quite severe.

TABLE XVII. COATINGS' COMPATIBILITY WITH ALAMAC H26D EMULSION, PR-1560M and PR-1005L (BUNA N) - EXPOSURE 28 DAYS @ 140°F			
Coating	Immersion	Pencil Hardness	Coating Condition
PR-1560M	JP-4	3H	No deterioration
	Alamac	HB	No deterioration
PR-1560M and PR-1005L (Buna N)	JP-4	HB	Topcoat (Buna N) turned brown
	Alamac	B6 ruptured topcoat	Topcoat (Buna N) turned dark brown
PR-1005L (Buna N)	JP-4	HB	Coating turned brown
	Alamac	-	Coating heavily blistered - peeled intact from panel

The test conditions follow:

PR-1560M Batch #LI-2110-3  
PR-1005L Batch #C-00254 (Buna N)

Type II anodized 7075-T6 aluminum panels, 2-3/4-in. x 6-in., were cleaned with methyl ethyl ketone and Table IV cleaner of MIL-S-8802C to prepare for coating application. One set of panels was dipcoated with PR-1560M, one set with PR-1005L, and another set with PR-1560M and a topcoat of PR-1005L. All PR-1560M-coated panels were cured 2 days at 77°F and 50% RH, then 1 day at 120°F; PR-1005L-coated panels were cured 3 days at 77°F and 50% RH. The three coatings systems were exposed to Alamac emulsion and JP-4 for 28 days at 140°F and then checked for coating condition. Pencil hardness of MIL-C-27725 was performed on each panel. Panels were run in duplicate.

#### 8.4 Groove Sealant

Two groove sealant candidates were applied, cured, and tested for resistance to Alamac H26D emulsion. JP-4 reduces the pressure at which failure occurs after a 7-day exposure at 140°F, and the emulsion causes still more deterioration as the data of Table XVIII indicate.

The test conditions follow:

Groove sealants - Q-94-011 Batch #080510  
PR-701-M Batch #C-70546

Specimens were prepared in triplicate and tested in the rupture jig of MIL-S-81323(WP). Slots were filled with sealing material and stabilized for 30 minutes. Excess sealant was trimmed with a razor blade, and the specimens were immersed in JP-4 and Alamac emulsion for 7 days at 140°F. Specimens were allowed to cool in the fluid and were tested upon removal by increasing 1/2 psig every 15 seconds. Data are shown in Table XVIII.

TABLE XVIII. GROOVE SEALANT COMPATIBILITY WITH ALAMAC H26D - 7-DAY EXPOSURE				
Immersion Data	0-94-011 Rupture (psig)		PR-701-M Rupture (psig)	
	Rep.	Avg.	Rep.	Avg.
None	18	19	8.5	8.5
	21		8.5	
	18		8.5	
JP-4	13.5	12.7	10.5	10.7
	12.5		10.5	
	12.0		11.0	
Alamac	3.5	3.8	2.0	1.7
	5.5		1.5*	
	2.5		1.5	
*PR-701-M sealant appeared to be swollen, color bleached to lighter grey.				

### 8.5 Elastomers

Buna N, Viton I, and fluorosilicone elastomer O-ring samples were exposed for 72 hours at 77°F to JP-4 and Alamac H26D emulsion with the results shown in Table XIX. Buna N, again, was most affected by the Alamac emulsion, the other elastomer values approximating that of JP-4.

The O-rings were the following:

MIL-P-5315 - Buna N  
MIL-R-25897 - Viton Class I  
MIL-R-25988 - Fluorosilicone

Volume change was determined in accordance with ASTM D 471-63T on triplicate O-rings immersed in JP-4 and emulsion for 3 days at 77°F. Hardness change is the difference of hardness readings taken (in accordance with ASTM D 676-59T) before and after immersion of the O-rings.

Tensile strength and ultimate elongation determinations were made in accordance with ASTM D 1414-56T on unexposed and on immersed O-rings.

TABLE XIX. ELASTOMER COMPATIBILITY - O-RING RESISTANCE TO JP-4 AND ALAMAC H26D, 72-HOUR EXPOSURE @ 77°F									
Type O-Ring	Immersion Medium	psi Tensile		% Elongation		% Volume Change		Hardness Change	
		Rep	Avg	Rep	Avg	Rep	Avg	Rep	Avg
Buna N	None	1510		239					
		1697	1613	259	250	-	-	-	-
		1632		252					
	JP-4	1252		213		11.2		-2	
		1318	1274	220	213	11.4	11.4	-2	-2
		1252		207		11.5		-1	
	Alamac	1413		239		19.1		-6	
		1462	1414	246	237	19.2	19.0	-3	-4
		1368		226		18.8		-3	
Viton I	None	1628		231					
		1738	1668	233	230	-	-	-	-
		1638		227					
	JP-4	1747		256		3.0		-1	
		1671	1733	232	253	2.7	2.9	-1	-1
		1780		272		2.9		0	
	Alamac	1404		214		4.4		-1	
		1714	1589	263	247	4.3	4.2	-3	-1
		1648		264		4.0		0	
Fluoro- silicone	None	719		138					
		645	636	121	122	-	-	-	-
		543		108					
	JP-4	373		88		12.4		-1	
		438	423	95	95	12.0	12.1	-1	-1
		458		101		12.0		0	
	Alamac	407		98		13.5		-1	
		424	433	98	101	13.8	14.0	0	-1
		468		108		14.7		-2	

## 9. Metal Corrosion Tests

In addition to the potential effect of JP-4 upon materials of construction of fuel tanks or systems, the combined effect of JP-4 and the emulsifier must be defined. In these tests, metals and elastomers were chosen which are the most commonly encountered in aircraft.

### 9.1 Single-Panel Tests

Metal strips, 1 in. x 3 in. (methanol- and acetone-cleaned), were immersed two-thirds of their length in various emulsions (4-oz jars) and observed at 77°F over a period of 30 days. The percentage of emulsion separation was monitored, and at the end of 30 days the metal strips were examined under 20X magnification for pitting or corrosion. The metals were given a numerical rating between 1 and 10 as to corrosion severity, and these are listed in Table XX. The high numbers (8-10) indicate severe corrosion over a general area, above and below the emulsion surface; 4-7 indicate light, general corrosion; and 0-3 indicate only a few small areas of light corrosion. The percentage of emulsion breakdown after 7 and 30 days is also reported in Table XX.

The corrosion test shows in general that JP-4 emulsions are less corrosive than straight JP-4, with magnesium being the only exception. Apparently, the small amount of free water in JP-4 is more harmful than the 1.5% which is tied up in the emulsions.

The emulsion stability test shows in general that the Alamac and Emcol emulsions are unaffected by most of the common alloys and metals used in the aircraft.

### 9.2 Metal Couple Tests

Metal strips were cleaned in methyl ethyl ketone and acetone, respectively. The two strips which were to make the couple were tied together with narrow strips of polyethylene so that half their lengths overlapped. The couples were completely immersed in both Ashland JP-4 and Alamac emulsion made from that JP-4. After 12 days at 77°F, the metals were removed from the fluids and examined for corrosion.

The test results showed (Table XXI) the following:

All the emulsions with bronze couples contained a purple powder, and the bronze strips contained strong multi-colored stains everywhere except for the parts in contact with the other metal. There was no discoloration of

TABLE XX. EFFECT OF VARIOUS EMULSIONS ON ALUMINUM ALLOYS AND OTHER METALS																
Metal rating (0-10) as to severity of corrosion - 30-day exposure																
Emulsion	Bare Al		Al Clad		H <sup>+</sup> Anodized		Bare		Al Clad		Bare		Steel		Titanium	
	2024	2024	2024	2024	2024	2024	7075	7075	7075	7075	7075	7075	6061-T6	AISI 4340	QQ-B-613	MIL-T-7993
JP-4 Straight	1	10	10	0	0	0	10	3	1	2	1	10	5	6	0	0
Emcol CS-136+TEA	0	2	0	0	0	0	1	0	0	2	1	1	6	1	0	0
Antara LE-600+TEA	1	10	10	0	0	0	10	3	0	0	0	1	7	3	0	0
Alamac H26D	1	3	0	0	0	0	5	2	0	1	1	1	10	5	0	0
Gafac RM-410+N-PA	1	0	0	0	0	0	8	2	0	1	1	1	9	1	1	1
Antara LP-200+TEA	1	10	10	0	0	0	1	4	0	3	0	0	8	4	0	0
Note: All aluminum was stained, worse from JP-4 than from emulsions.																
EFFECT OF VARIOUS METALS ON EMULSION STABILITY AFTER 30 DAYS																
% of free JP-4 fuel																
Emulsion	Bare Al		Al Clad		H <sup>+</sup> Anodized		Bare		Al Clad		Bare		Steel		Titanium	
	2024	2024	2024	2024	2024	2024	7075	7075	7075	7075	7075	7075	6061-T6	AISI 4340	QQ-B-613	MIL-T-7993
Emcol CS-136+TEA	0	1	0	0	0	0	0	0	0	0	5 (4)*	0	40 (3)	25 (5)	0	0
Antara LE-600+TEA	0	0	0	0	0	0	0	0	0	10 (5)	0	0	60 (30)	50 (10)	0	0
Alamac H26D	0	0	0	0	0	0	0	0	0	15 (3)	0	0	98 (80)	98 (40)	10 (0)	0
Gafac RM-410+N-PA	0	0	0	0	0	0	0	0	0	0 (0)	0	0	80 (70)	10 (0)	0	0
Antara LP-200+TEA	0	0	0	0	0	0	0	0	0	5 (2)	0	0	95 (50)	90 (30)	5 (0)	0
*( ) - % JP-4 after 7 days.																

bronze in JP-4. None of the other metals in any of the couples showed any sign of corrosion in either the emulsion or the JP-4. Bronze and stainless steel caused the emulsion to break on immediate contact with them, while the aluminum alloys had no effect.

TABLE XXI. METAL COUPLE CORROSION TESTS	
Metals	Couples
Bronze	Bronze-Anodized 2024
304 Stainless Steel	Bronze-6061
Bare 6061 Aluminum	Bronze-S.S.Steel
Bare 6061 Alodined	S.S.Steel-6061
Bare 2024-T3 Anodized (H <sub>2</sub> SO <sub>4</sub> )	S.S.Steel-Alodined 6061

## 10. Lubricity

The lubricity of the Alamac emulsion, of the JP-4 from which it was made, and of JP-4 recovered from the emulsion was determined using the Shell Four-Ball tester and technique. The two pertinent values used for comparison are the wear scar diameter and the coefficient of friction. These values for the "as received" JP-4 and those for the recovered JP-4 are essentially equal, indicating no change in the lubricity characteristics of the two fuels. The values for the emulsion were significantly lower, showing less wear and a lower coefficient of friction. Table XXII provides the data from which Figure 9 was developed. The slopes of the curves are 1.30 for the emulsion, 0.313 for the "as received" JP-4, and 0.328 for the recovered JP-4. Although the JP-4 values are greater than the 0.25 slope reported for some JP-4's, these values show the significant difference between the fuels and the emulsion.

## 11. Static Charge

### 11.1 Conductivity

Electrical conductivity measurements were made on three emulsions via the conductivity cell method. The conductivity cell used was a glass container of approximately 100-milliliter capacity and a set of concentric cylindrical electrodes.



TABLE XXII. FOUR-BALL WEAR TESTS						
Time (Min.)	Wear Scar Diameter, In.				Torque	Coefficient of Friction
	#1	#2	#3	Avg, mm		
<u>JP-4</u>						
0.1	0.0090	0.0087	0.0083	0.0221	-	-
0.2	0.0092	0.0086	0.0075	0.0214	-	-
1.0	0.0107	0.0104	0.0106	0.0269	10.0	0.224
5.0	0.0179	0.0174	0.0183	0.0453	12.0	0.268
10.0	0.0190	0.0210	0.0199	0.0508	15.0	0.334
30.0	0.0335	0.0330	0.0338	0.0849	15.0	0.334
<u>Recovered JP-4</u>						
0.1	0.0077	0.0074	0.0073	0.0190	-	-
0.2	0.0089	0.0123	0.0082	0.0249	-	-
1.0	0.0109	0.0117	0.0103	0.0279	10.0	0.224
5.0	0.0179	0.0174	0.0183	0.0453	12.0	0.268
10.0	0.0190	0.0210	0.0199	0.0508	15.0	0.334
30.0	0.0335	0.0330	0.0338	0.0849	15.0	0.334
<u>Emulsion</u>						
0.1	0.0076	0.0077	0.0083	0.0201	-	-
0.2	0.0095	0.0096	0.0100	0.0246	-	-
1.0	0.0107	0.0106	0.0109	0.0272	6.0	0.134
5.0	0.0143	0.0127	0.0139	0.0345	8.0	0.178
10.0	0.0167	0.0155	0.0168	0.0414	10.0	0.224
30.0	0.0137	0.0136	0.0142	0.0351	10.0	0.224

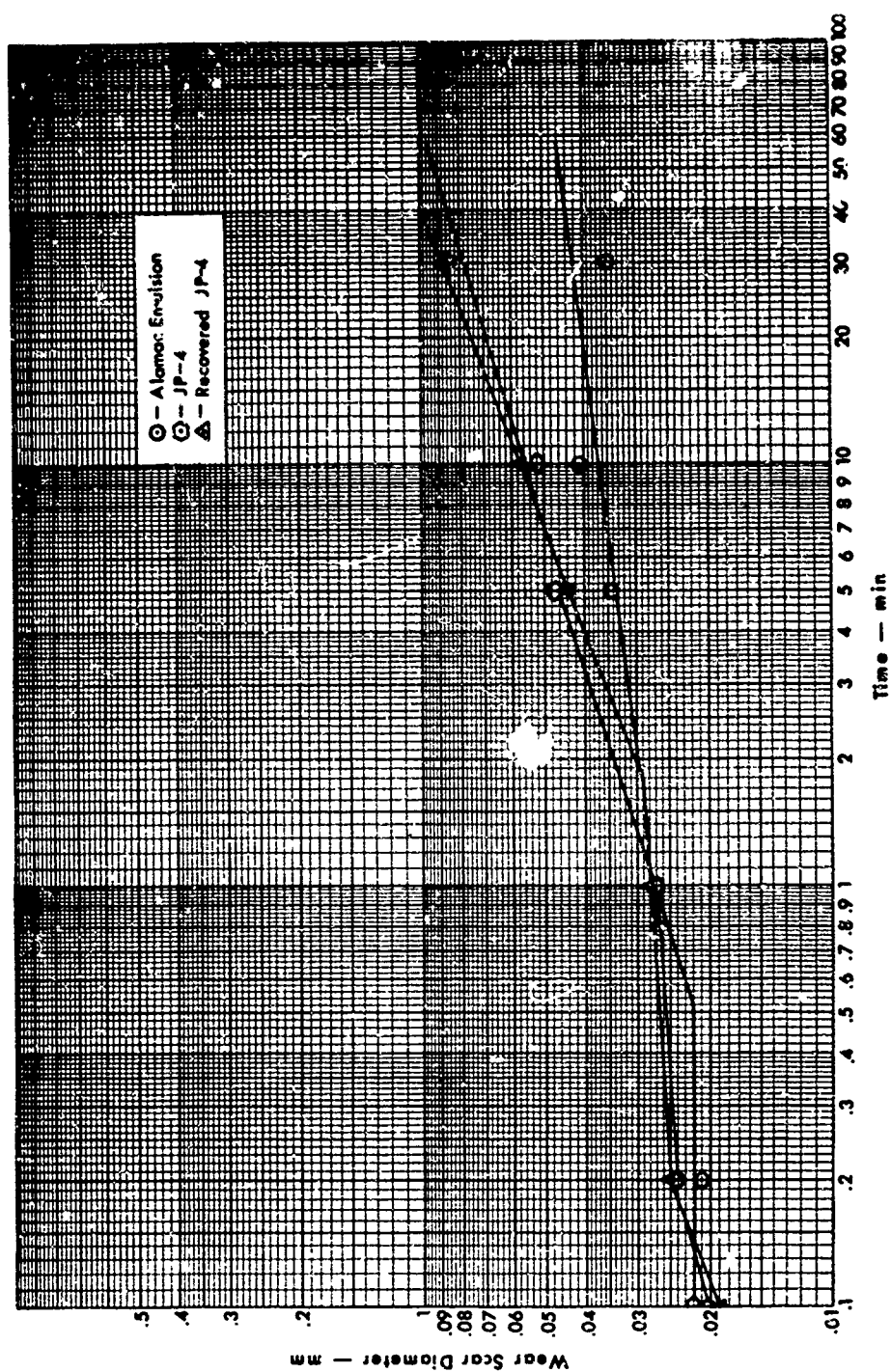


Figure 9. Lubricity.

About 40 milliliters of the emulsion were placed in the container and the electrodes were immersed. They were connected in series to a 1.5-volt dry cell and Keithley Model 200 Electrometer with a Model 2008 Decade Shunt top-mounted. All the equipment was set up in a grounded Faraday Cage made of heavy, 4-mesh copper screen. Conductivity was calculated by Ohm's law from the current, applied voltage, and known characteristics of the cell.

The data of Table XXIII show that the fuel emulsions are much more conductive than straight JP-4 fuel and hence will cause less static buildup.

TABLE XXIII. CONDUCTIVITY	
Fuel	Conductivity, mho/cm
JP-4	$8.5 \times 10^{-14}$
Emcol CS-136	$2.1 \times 10^{-8}$
Antara LE-600	$2.5 \times 10^{-8}$
Alamac H26D	$4.1 \times 10^{-8}$

The units in which conductivity are usually expressed<sup>4</sup> are rather cumbersome when very low conductivities must be denoted. This is the case with petroleum products, where powers of ten with large negative exponents are common. For simplification, conductivity units may be used which are:

$$1 \text{ picomho/meter} = 10^{-12} \Omega^{-1} \text{ m}^{-1} = 10^{-14} \Omega^{-1} \text{ cm}^{-1}$$

The electrical conductivity needed for adequate removal of charge from a liquid depends on the rate of charge generation. A conductivity of at least 50 conductivity units is sufficient for most refinery operations. However, in cases such as fueling jet aircraft, a conductivity of 500 conductivity units is required.

The base JP-4 used in preparing the emulsified fuel had a conductivity of 8.5 conductivity units, which falls well within the range of light distillates of 0.01 to 10 conductivity units. The conductivity for the fuel emulsion was 4.1 million conductivity units, which falls between the

conductivity of distilled water (100 million conductivity units) and that of light distillates. The conductivity of the emulsion significantly exceeds the requirements for aircraft fueling stated above, indicating that static charge is very unlikely to be a factor in emulsion transfer.

### 11.2 Static Electricity Generation

It is well known that jet fuel becomes electrically charged when pumped from point to point. This charge may be generated during ground handling operations as well as during internal fuel transfer of aircraft in flight.

The objectives of this work were to establish the static electricity-generating characteristics of Alamac emulsion and to compare the fuel emulsion properties to those of the base JP-4 and those of JP-4 recovered from the emulsion.

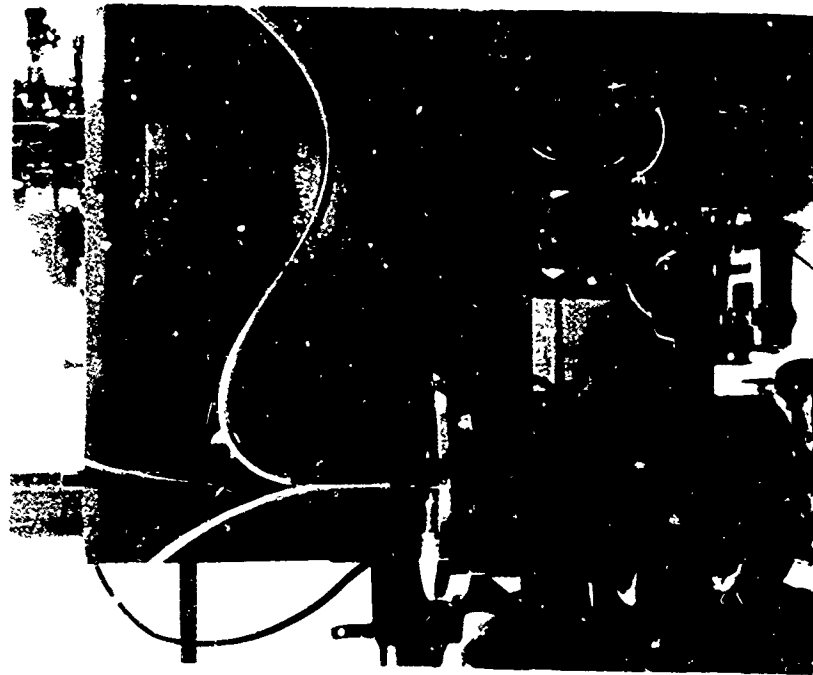
The experimental apparatus (Fig. 10-B) involved the production of frictional contact between the fuels and metallic surfaces and the measurement of the generated electrical current flowing to the ground from an insulated length of stainless steel tubing (Fig. 10-A). The current-measuring instrument used was a Keithley Model 2008 Decade Shunt. A variable-speed pump (0-580 ml/min) was used to circulate the fuels through a closed loop. Current measurements were made at various fuel flow rates and are graphically shown in Figure 11.

Both JP-4 fuels had similar electrostatic characteristics, while the Alamac emulsion generated essentially no current at the maximum flow rate investigated.

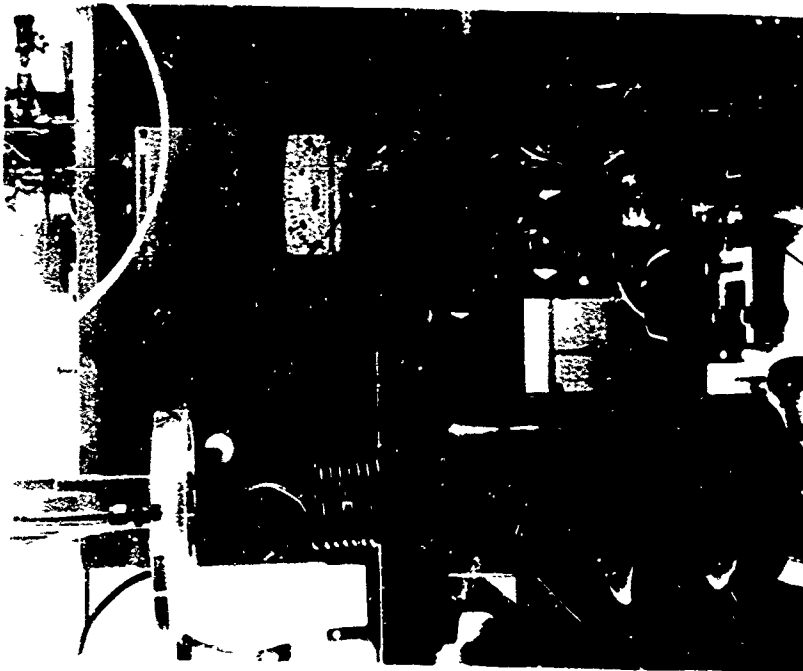
During the fuel emulsion tests, it was found that emulsion collected in the 90° elbow returning to the pump. This emulsion did not interfere in any way with the pumping but could not be washed out with JP-4 at test completion. The entire system had to be disassembled before thorough cleaning was accomplished.

### 11.3 Static Charge Stability

A glass-insulated buss wire was centered in a stainless steel beaker. The buss wire was then connected in series with a 10-megohm, 2-watt resistor to the positive terminal of a Model 711, Hewlett-Packard variable power supply (range 0-500V DC). The negative side of the power supply was connected to the beaker and grounded. A 300V potential was



A



B

Figure 10. Static Buildup Apparatus.

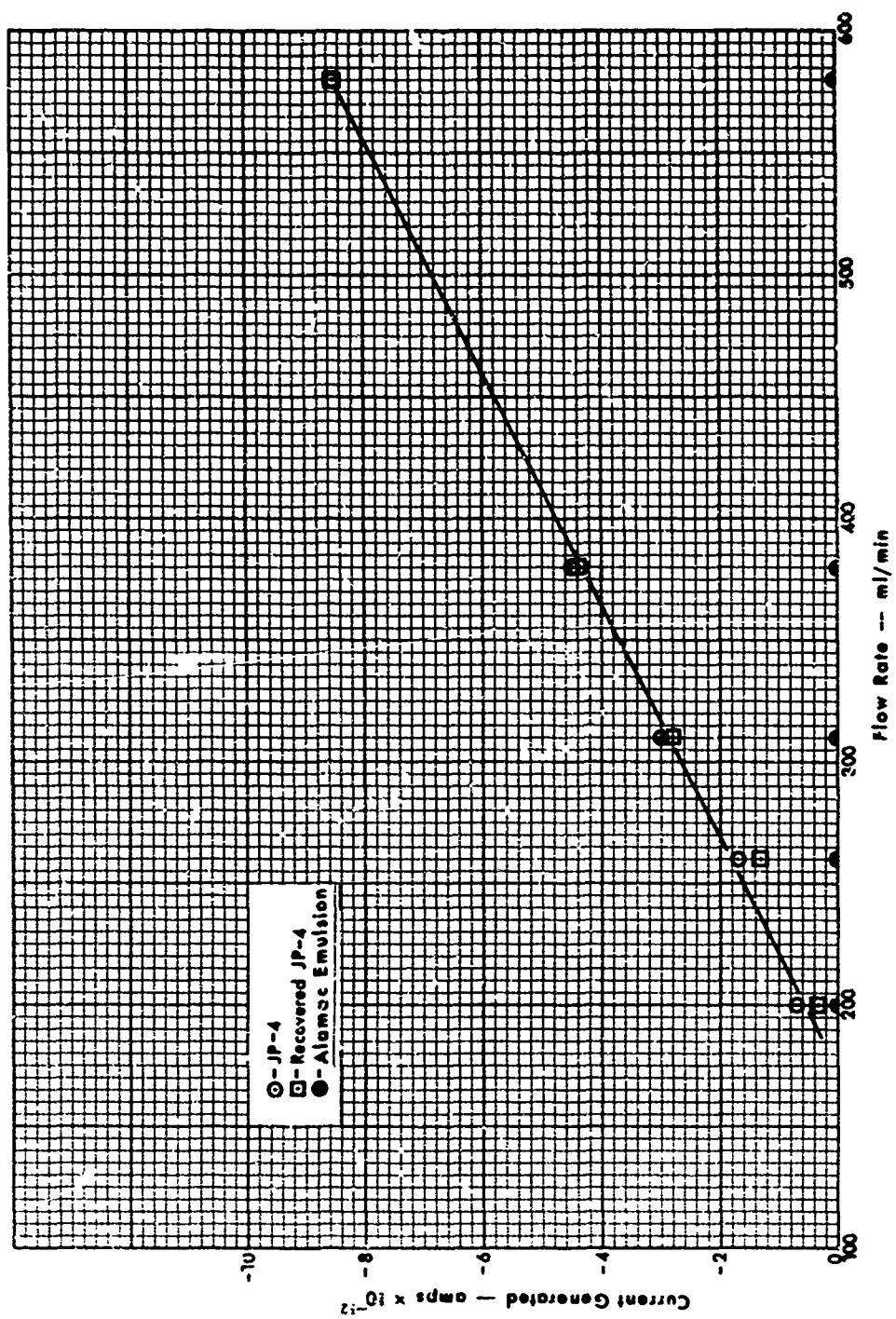


Figure 11. Electrostatic Charge Generation.

impressed across the beaker/buss wire (filled with fuel emulsion) for a 3-hr period. No fuel or external-phase migration was observed.

## 12. Microbiological Tests

Biocides which had been demonstrated as effective against microbiological deterioration of JP-4 fuel were chosen for this work, based upon their ionic activity. Since incompatibility exists between anionic and cationic agents, a cationic type was chosen for the Alamac emulsion, and an anionic type for the Emcol emulsion. These biocides were:

Alamac - Isothan Q-75 (N-alkylisoquinolinium bromide)  
from Onyx Chemical Company

Emcol - Dioxin (6-acetoxy-2,4-dimethyl-n-dioxane)  
from Sindar Division

It should be noted at this point that the main ingredient of the anti-icing additive used in JP-4, methyl cellosolve, has been shown to be an effective biocide. Since it is normally present in the fuel, it may prove to be adequate protection as well as to act as an emulsion stabilizer.

### 12.1 Compatibility With Biocides

The two biocides were mixed with several emulsions at a concentration of between 0.006-0.012% in the finished emulsion (2-4000 ppm based on external phase).

About 100 milliliters of Alamac H26D, Emcol CS-136, and Antara LE-600 emulsions with the biocides were stored at 135°F for one week and observed for stability as percent broken emulsion.

<u>Biocide</u>	<u>Emcol CS-136</u>	<u>Antara LE-600</u>	<u>Alamac H26D</u>
Dioxin	0	0	2%
Isothan Q-75	2%	0	0

For the Alamac emulsion, the Isothan agent appeared to be the most compatible, and was used in subsequent tests.

## 12.2 Microbiological Data

Two fuel-utilizers (*Pseudomonas* and *Hormodendrum* spp.) and two nonfuel-utilizers (*Staphylococcus* and *Bacillus* spp.) were tested for their ability to grow and survive in test systems composed of emulsified and nonemulsified forms of JP-4 jet fuel. Neither emulsion (Alamac #1 or Alamac #2) supported microbial growth in the absence of a water phase. Growth of *Ps. aeruginosa* in liquid systems with either emulsion was not significantly different from growth in liquid systems with nonemulsified fuel. Growth of the *Hormodendrum* sp. in systems containing the emulsions was less than in systems containing JP-4 fuel, but good growth was noted on spread plates of the systems with both emulsions. The responses of *Staphylococcus* and *Bacillus* spp. in systems containing fuel emulsions were similar to responses of these organisms in systems with JP-4 fuel. Complete data are shown in Appendix VI.

## 13. Pumpability

Figure 12 shows the nonwetting character of the CS-136 emulsion and that it can be broken into separate streams during transfer.

Figure 13 shows a comparative "slump" of the two emulsions after 5 minutes. The "slump" of the 2-in.-diameter plugs of emulsion corresponds to the relative emulsion viscosities. The surface upon which the plugs were placed was glass.

## 14. Methods of Emulsification

### 14.1 Pump Emulsification

Laboratory-scale experiments were set up to determine if the stirring action caused by a circulating pump was sufficient to completely emulsify a mixture of 25% premix emulsion and the other 75% of the JP-4. Emcol CS-136 + TEA was the chosen surfactant.

#### 14.1.1 Gear Pump

A small, low-capacity gear pump operated by a 1700-rpm motor was tried first. A vertical 2-in. pipe, long enough to hold a liter of emulsion, was mounted on the 1/4-in. pump inlet. The outlet end from the pump was fitted with open 1/4-in. tubing for recycle purposes. The Emcol CS-136 premix with



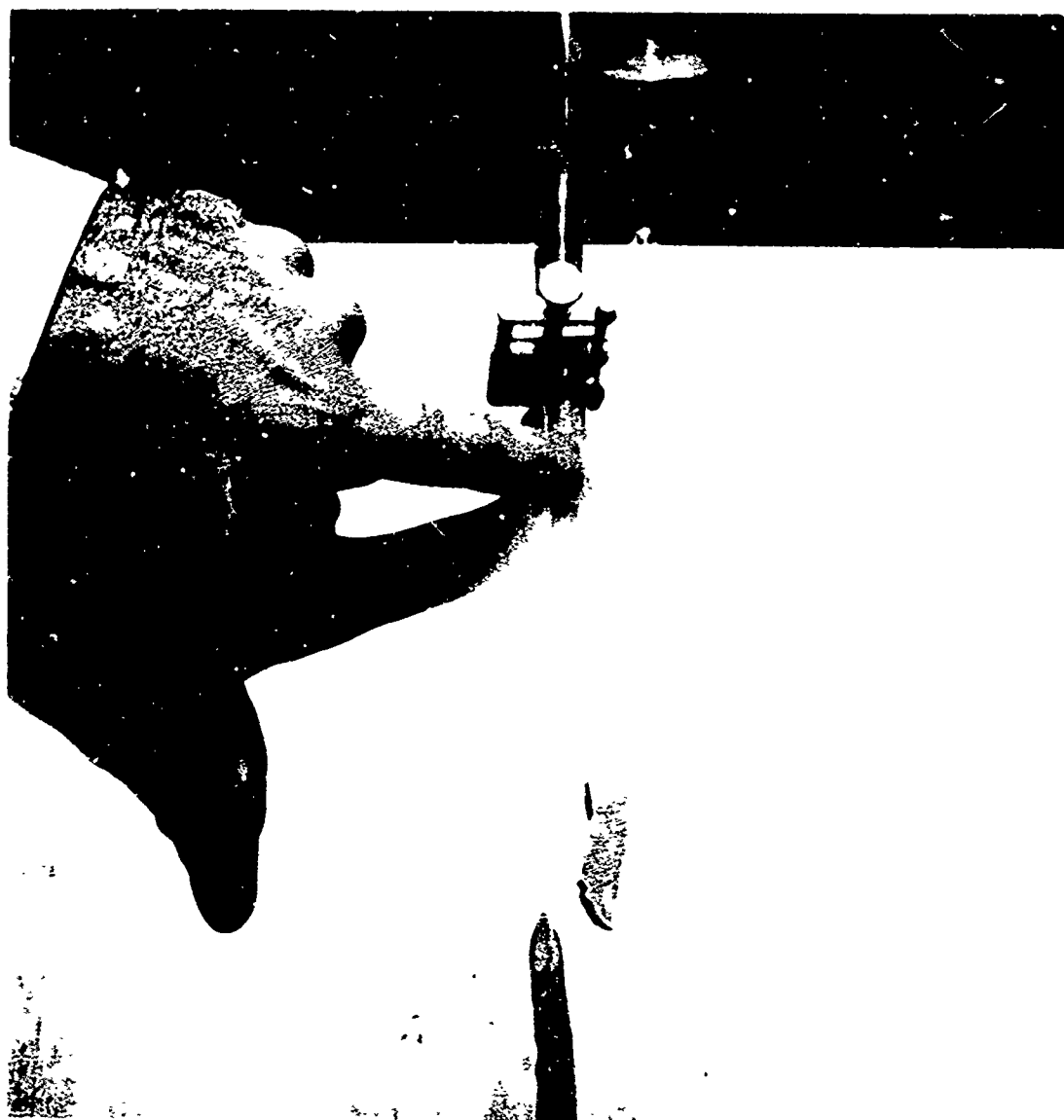
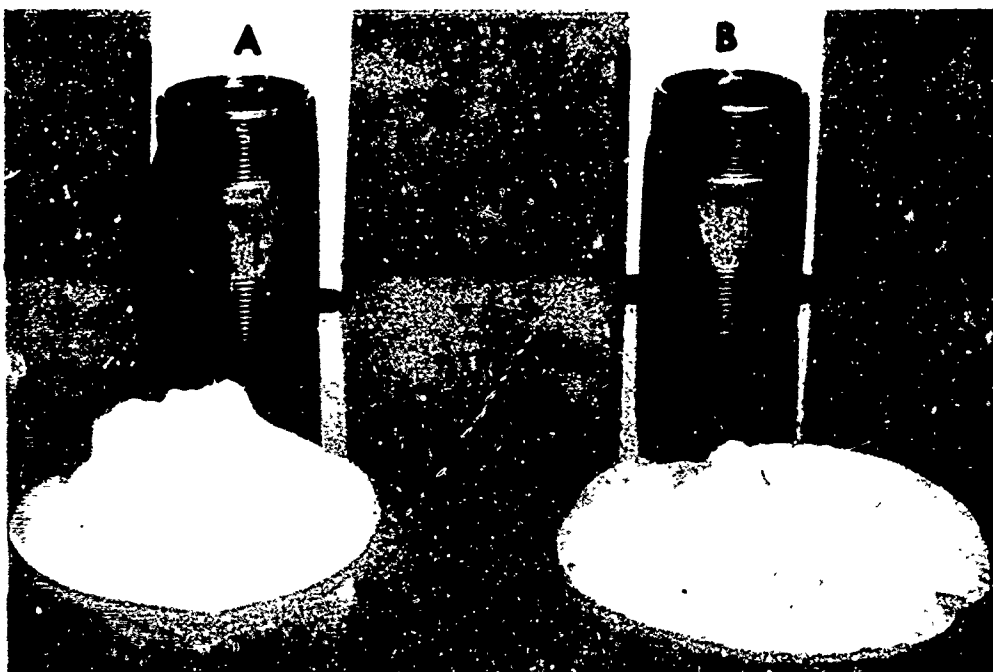


Figure 12. Pumped CS-136 Emulsion.



A - Emcol CS-136 Emulsion  
B - Alamac H26D Emulsion

Figure 13. "Slump" of JP-4 Emulsions.

JP-4 fuel was poured into the inlet pipe and the pump was started. At first, the two components were mixed together as they both went through the pump. However, after a few cycles, the premix floated to the top of the inlet pipe and only the JP-4 continued circulation. Apparently, the pump was too small to create enough turbulence for sufficient mixing.

#### 14.1.2 Centrifugal Pump

A high-speed, 3400-rpm centrifugal pump with Variac voltage control was piped similarly to the gear pump apparatus. The only difference was that the inlet, outlet, and return line were of 3/8-in. piping instead of 1/4-in. tubing. The motor speed was operated at a slow range, and the complete emulsion nearly formed, with about 95% of the fuel emulsified. However, at this point, the emulsion became chunky and the pump cavitated. An increase in pump speed started the emulsion flow again, but also started to break it down into free fuel. Several additional attempts resulted in either pump cavitation or the floating premix problem.

This one test demonstrated that this type of mixing action can produce an emulsion provided the above-mentioned problems can be overcome.

#### 14.2 Other Mixers

##### 14.2.1 Dispersator Mixers

Paint companies use large-scale Dispersator mixers. A laboratory model of this equipment was secured for trial. The Dispersator mixer incorporates a rotating circular disc or cylindrical tube with perpendicular circumferential saw-teeth. Attempts were made to prepare Emcol CS-136 emulsion at both 3400 and 1200 rpm; however, both speeds proved to be too high to start the emulsification process. When a one-shot fuel addition was made to a 10% premix at the 3400-rpm speed, no additional emulsion formed. With slow fuel addition to the premix at 1200 rpm, the emulsion formed until about half the JP-4 had been added. At this point, the emulsion became chunky and rubbery and would not mix with additional JP-4.

Attempts were then made to prepare the emulsion at a paint company, which also had a lab-scale Dispersator-type mixer but with variable speed as low as several hundred rpm. Even this low speed proved to be too rapid for initiating the emulsion, and a 10% premix had to be used. Additional JP-4

was added slowly at low speed, and the emulsion became chunky and rubbery after about half the JP-4 had been added. No additional JP-4 would mix, even by rotating the container.

When a one-shot JP-4 addition was made to the 10% premix, the emulsion became slightly chunky, then continued to a moderately smooth emulsion, but the remaining JP-4 would not emulsify. It was therefore concluded that a full-scale mixer of this type could not be used for emulsion preparation. The attempts are shown in Table XXIV as 46-22, 46-28, 46-29, and 46-30.

Emcol CS-136 emulsion was prepared with the very slow speed of the Lightnin' mixer when a one-shot JP-4 addition was made to 10% premix. However, the container had to be rotated by hand so that the mixer blade covered nearly all the volume in the container. The emulsion was unsuccessful.

#### 14.2.2 Olsen & Tilgner Paint Mixer

An Olsen & Tilgner Paint Mixer (pony-type) was used to prepare emulsions. This mixer had a 3-gallon capacity but utilized the desired planetary type of motion for mixing. The mixer head consisted of four evenly spaced bars dropped vertically from and perpendicular to a rotating wheel. The wheel rotated at 60 rpm, while the mixer bowl rotated at about 30 rpm. When a one-shot JP-4 addition was made to a 10% premix, no additional emulsion formed. When the JP-4 was added slowly to the premix, additional emulsion formed. However, the low speed of the mixer required nearly four hours of mixing time, and then the final emulsion was noticeably thinner than normal. When examined under the microscope with emulsion made with the Hobart mixer, the thin emulsion was found to contain much larger droplets, which slowly coalesced under the pressure of sandwiching between two glass slides. It was estimated that 35% of the volume of the thin emulsion was occupied with droplets of size 30-40-micron diameter, and 65% with droplets of normal 5-10-micron size. The speed of this mixer was too slow to form the emulsion properly, although it did meet thermal stability requirements (tests 46-26 and 46-27 of Table XXIV).

A local paint company was visited in the search for an acceptable large-scale mixer. Various small mixers in their laboratory, which were known to correlate with production mixers, were used in making emulsions. The results were as follows.

TABLE XXIV. MIXER EVALUATION					
No.	Surfactant Name	External Phase			Preparation and Stability
		Wt. % Surf.	Vol. % Water	Vol. % Et. Glycol	
46-14	Fmcol CS-136	1.10	5.05	5.05	25% premix preparation, Lightnin' mixer; stable at 80° for at least 7 days
46-15	Emcol CS-136	2.40	11.0	11.0	10% premix preparation, Lightnin' mixer; little entrapped air, could be metered
46-16	Emcol CS-136				10% and 25% premix preparations, Hobart mixer; much entrapped air, hard to meter
46-17	Emcol CS-136	0.30	1.37	1.37	Hobart mixer, 25% premix added to stirred JP-4; required 10 min of stirring, emulsion stable
46-18	Emcol CS-136	0.30	1.37	1.37	Hobart mixer, 10% premix, one-shot JP-4 addition, required 8 min of stirring, emulsion stable
46-19	Amara LE-600	0.40	1.30	1.30	" " " " " " " "
46-20	Alamac HP-6D	0.30	1.27	1.37	" " " " " " " "
46-19	Emcol CS-136	0.30	1.37	1.37	Hobart mixer, 10% premix made with <u>Lightnin'</u> ; required 30 min because of lack of air
46-20	Emcol CS-136	0.30	1.37	1.37	Hobart mixer, 10% <u>Lightnin'</u> premix beat 1 min in Hobart; required only 10 min
46-21	Emcol CS-136	0.30	1.37	1.37	Lightnin' mixer, 10% premix, bowl moved by hand; required 60 min for one-shot JP-4 addition
46-22	Emcol CS-136	0.30	1.37	1.37	3400-rpm Dispersator mixer, 10% Lightnin' premix, one-shot JP-4 addition, no emulsion formed
46-23	Emcol CS-136	0.30	1.37	1.37	1200-rpm Dispersator mixer, 10% Lightnin' premix, JP-4 added slowly, emulsion would not finish after 50% added
46-24	Emcol CS-136	0.30	1.37	1.37	ca. 300-rpm Dispersator mixer, 10% premix, JP-4 added slowly, emulsion would not finish after 50% added
46-25	Emcol CS-136	0.30	1.37	1.37	ca. 300-rpm Dispersator mixer, 10% premix, one-shot JP-4 addition, only 95% of emulsion formed
46-26	Emcol CS-136	0.30	1.37	1.37	Olsen & Tilghner Paint Mixer, 10% Lightnin' premix, JP-4 added slowly 4 hrs, 5% JP-4 after 7 days @ 135°P
46-27	Emcol CS-136	0.30	1.37	1.37	Olsen & Tilghner Paint Mixer, 10% Lightnin' premix, one-shot JP-4 addition, no emulsion formed
46-28	Emcol CS-136	0.30	1.37	1.37	Hobart, CS-136 and TEA dissolved faster in water and glycol <u>unreacted</u> , emulsion stable and normal
46-29	Emcol CS-136	0.30	1.37	1.37	Prepared in situ with TEA in H <sub>2</sub> O, CS-136 in JP-4; slower than usual, emulsion stable
46-30	Amara LE-600	0.40	1.30	1.30	Hobart, LE-600 and TEA dissolved faster in water and glycol <u>unreacted</u> , emulsion stable and normal
46-30	Emcol CS-136	0.30	0.74	0	7 days @ 75°P - 10% JP-4 separated; 7 days @ 135°P - 2% JP-4 separated

#### 14.2.3 Double-Bladed Pony Mill (1-Gallon Capacity)

A 10% premix was used, and the rest of the JP-4 was added in about 10 minutes. The double blades produced good mixing action, although a little faster speed would have been desirable. The finished emulsion did not seem as fluffy as the Hobart mixer emulsion; however, the emulsion survived all the stability tests. It was found that the company no longer had production-size mixers of this type.

#### 14.2.4 Air-Driven Lightnin' Mixer

This Lightnin' mixer was different from the usual in that it utilized a rotating stirrer which caused stronger vortexing of the mixture. This stirrer consisted of a "paddle wheel" with a circumferential band. A 10% premix was used and the emulsion was prepared only by rotating the container. The emulsion process was slow, and there still remained a thin film of JP-4 on the container at the finish. This emulsion began to break after only one day at 75°F (46-38, Table XXV).

#### 14.2.5 Sigma Blade Stirrer (1/4-Gallon)

A 10% premix was used and a small amount of JP-4 was added. The action of the blades was much too slow and the emulsification was very slow.

### PART IV. EMULSION MANUFACTURE AND RECONSTITUTION

#### 1. Large-Scale Emulsion Manufacture

##### 1.1 Tower Paint Company Trial

A single-action, 70-gallon-capacity mixer was available at this local paint company. Attempts were made at preparing 50-gallon batches of Emcol CS-136 emulsion, using an 8.2% and 6% premix technique. However, complete emulsification was impossible to attain, and this fault was attributed to ineffective mixer action. Subsequent 2-gallon batch testing of this emulsion demonstrated that the fault lay not in the mixer, but in the sensitivity of this emulsifier to the low temperature of the JP-4 at the time of manufacture (see following Emcol CS-136 Emulsion Section). The data secured from the Tower Paint trial are given as Appendix IV.

TABLE XXV. MIXER EVALUATION						
Surfactant No.	Name	External Phase			Preparation and Stability	
		Wt. % Surf.	Vol. % Water	Vol. % Et. Glycol		
46-37	Emcol CS-136	0.3	1.37	1.37	Lowe Brothers Paint Co.; Double-bladed pony mixer (top speed) - stable emulsion.	
46-38	Emcol CS-136	0.3	1.37	1.37	Lowe Brothers Paint Co.; Lightnin' mixer with special "vortex-producing" blade; Stability: 77°F, 1 day - 1% JP-4, 6 days - 5% JP-4	
46-39	Emcol CS-136	0.3	1.37	1.37	Lowe Brothers Paint Co.; Sigma blade stirrer - too slow to produce stable emulsion.	

## 1.2 Hobart Mixer Manufacture

Since none of the large-scale mixers in the local area proved to be satisfactory, two Hobart Model C-100 mixers were used to prepare large quantities of emulsion for shipment. These mixers have an operating capacity of 6400 cc (1.7 gallons) and utilize planetary motion with an option of three speeds:

Speed Setting No.	<u>1</u>	<u>2</u>	<u>3</u>
Clockwise Beater Rotation, rpm	157	280	500
Counterclockwise Beater Translation, rpm	63	112	200

To simplify operations, external-phase concentrates (EPC) were made combining the emulsifier, ethylene glycol, and biocide (a 1-gallon volume is sufficient to prepare 35 gallons of emulsion). Water was added separately.

## 1.3 Emcol CS-136 Emulsion

### 1.3.1 External-Phase Concentrate (EPC)

The EPC was prepared by dissolving the Emcol CS-136 acid in the other ingredients, adding the calculated amount of triethanolamine (TEA) to give a neutral solution. When the emulsifier was neutralized in the water-glycol mixture, separation occurred, but this was prevented when the glycol was used first, adding the water after the neutralization in glycol. The added biocide, Dioxin, is an acetic acid ester which hydrolyzes in water; therefore, an additional calculated amount of TEA was added for neutralization.

### 1.3.2 Large-Scale Preparation

Large-scale manufacture was initiated with a 30-gallon quantity which appeared entirely satisfactory overnight. A further 10-gallon quantity was added to the drum. When added to the previous batch, another 10-gallon quantity resulted in a 1-inch separation of JP-4. Evaluation of the retained samples of the last 10-gallon production gave yield values of 3300 dynes/cm<sup>2</sup> and a particle size range of 3-10 microns, both essentially normal.



### 1.3.3 Temperature Sensitivity

Attempts then were made to determine the cause of poor quality emulsion. Variables investigated were the effects of: Dioxin with and without added TEA; method of preparation of the EPC; rate of JP-4 addition; method of emulsification; temperature; 33% increase in emulsifier; and presence or absence of anti-icing additive.

Table XXVI shows the variations observed and the data obtained. Test 1 shows that the Dioxin appeared not to be a controlling factor. Test 2 shows that method of EPC preparation, rate of JP-4 addition, and insufficient emulsifier were not the cause for instability. Test 3 shows that the separation was not attributable to method of preparation. The effect of JP-4 temperature and type (i.e., whether En-Ar-Co or Air Force supplied JP-4) prepared in the original small quantities, but with all materials at 77°F, indicated no real difference in any of the materials' variables (Test 4). However, Test 5 showed definitely that the JP-4 temperature (67° vs 77°F) controlled emulsion stability, the lower temperature production being less stable. The large-scale batches, prepared at <60°F, showed rapid instability, and this temperature accounts for the lack of stability of these large-scale Emcol emulsions.

Another minor difference was noted, in that emulsions made with JP-4 containing anti-icing additives (AIA) were more viscous than those not containing it. Qualitative tests indicate that the large-scale emulsions made from En-Ar-Co fuel are AIA-free.

Because of the temperature sensitivity of the Emcol emulsifier, along with other deficiencies, this system will no longer be investigated.

### 1.4 Alamac H26D Emulsion

#### 1.4.1 External-Phase Concentrate

The Alamac H26D surfactant was prepared by reacting Alamine H26D (tallow amine) with glacial acetic acid. The product never completely dissolved in the external phase, but was uniformly dispersed if the external phase was heated. The preferred method of preparation is to add the melted amine (130°F) to the acetic acid dissolved in the glycol. This method was used for the external-phase preparation, and the biocide, Isothan Q-75, was then added. The water was added separately during batch preparation because it reduces the Alamac solubility in the EPC.

TABLE XXVI. EMCOL EMULSIGN PREPARATION VARIABLES

Note: Tests 1, 2, and 3 are in the 2-gallon Hobart mixer. Tests 4 and 5 are in the 2-quart Hobart Kitchen Aid Mixer.

## TEST

## #1 (1-10-67)

	A	B	C		E
External Phase*	No Dioxin, TEA, glycol, Emcol, water	Dioxin added right after TEA	Dioxin excess TEA	#3 jug from 100-73 prep, Dioxin	Made fresh same as E
ph	← weakly basic →				
Emulsion Yield Stress	3300	3300	3500		-
Stability 1 Day	2% JP-4	2% JP-4	2% JP-4	1% JP-4	2% JP-4

## #2 (1-12-67)

	A	B	C	D	E	F
External Phase	Emulsifier premixed, no Dioxin	33% excess emulsifier no Dioxin	Fresh std same as #1 - D&E	Standard excess TFA	Emul. premixed reagent glycol no Dioxin	E external phase, all JP-4 added slowly
Stability 1 Day	NC	NC	NC	NC	NC	NC
8 Days	Syn**	1% JP-4	Syn	Syn	Syn	Syn

## #3 (1-13-67)

	#1D	#1D	2D	2D	1A	1E	2A
1 Day Later							
External Phase	Person A	Person B	Person A	Person B	Person B	Person B	Person B
Stability 3 Days	NC	NC	NC	NC	NC	NC	NC
7 Days	Syn	NC	NC	Heavy syn	NC	NC	NC
14 Days	Syn	Syn	Syn	Syn	Syn	Syn	Syn

## #4 (1-19-67)

	A		B		C		D		E	
External Phase	Emul. premixed no Dioxin		(A) all JP-4 added slowly		(A) but Dioxin added		#1D		(A) but with AP JP-4	
Stability 135°F	77°F	135°F	77°F	135°F	77°F	135°F	77°F	135°F	77°F	77°F
3 Days	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
7 Days	Syn	Syn	Syn	NC	Syn	NC	Syn	NC	Syn	NC

## #5 (1-20-67)

	A		B	
External Phase	Emul. premixed no Dioxin		#1D	
Stability 135°F	77°F	135°F	77°F	77°F
3 Days	Syn	NC	Syn	NC
7 Days	1% JP-4	Syn	2% JP-4	Syn

\*Prepared the standard method as mentioned in report, with exception mentioned in table.

\*\*Synthesis - a few droplets of fuel.

#### 1.4.2 Large-Scale Preparation

Volumes of 110 milliliters of EPC and 88 milliliters of water were added to the mixing bowl. The Alamac precipitated at first but later dissolved when the JP-4 was added. The same method of JP-4 addition was used as in the Emcol emulsion, and the first emulsion was prepared with 45°F fuel. This JP-4 had to be added more slowly than normal, but the emulsion was quite stable.

#### 1.4.3 Shipment to Falcon Research & Development Co.

Four 50-gallon lots of Alamac emulsion were prepared. Lot samples of 2-oz size were taken from each batch of drums 1 and 2, and 1-gallon composite lot samples were taken from drums 3 and 4. The individual lot samples were stored at 135°F for 7 days, and the gallon composites were stored at 77°F. Yield values were determined periodically during manufacture, and these ranged from 1400 to 2600 dynes/cm<sup>2</sup>, with the median value around 2100 dynes/cm<sup>2</sup>. The lower values were obtained after storage for up to 24 hours.

The four drums of Alamac emulsion were dated, labeled, and sent to Falcon Research & Development Co., Denver, Colorado.

#### 1.4.4 Shipment to Allison Division

Two hundred gallons of Alamac emulsion were shipped to Allison for bench testing. This amount was prepared with the 1.7-gallon (6400 ml) Hobart mixers, and was stored and shipped in air-dried, 55-gallon JP-4 drums.

The method of preparation was essentially identical to that previously mentioned for the emulsion sent to Denver, Colorado. The total mixing time was reduced from 20 minutes to 18 minutes, and all the final JP-4 was added during a period of 4-6 minutes instead of the previous 10 minutes. The ethylene glycol external-phase concentrate (glycol, Alamac, biocide) was prepared identically, and the same quantity of 110 ml was used in every batch. The amount of water added was reduced from 88 ml to 84 ml, so that the total external phase amounted to exactly 3.0 volume %. The previous emulsion contained 3.06% external phase because an adjustment was not made for the 5:4 volume-weight ratio of Alamac H26D.

JP-4 from the National Refining Company again was used for the emulsion preparation. This also did not contain (by qualitative examination) the anti-icing additive which would have aided the emulsion. Since the methyl cellosolve was

claimed to have been added, it is theorized that perhaps excess water in the JP-4 in refinery storage extracted the additive.

Periodic yield stress measurements on individual batches of emulsion immediately after preparation averaged 2800 dynes/cm<sup>2</sup>, higher than the previous 2100 dynes/cm<sup>2</sup>. Composite samples were taken for each drum of emulsion and passed the one-week stability test at 135°F.

The emulsion in the 55-gallon drums was observed daily while awaiting shipment. After about 3 days, a film of JP-4 appeared at the drum-emulsion-vapor interface. This film slowly widened as time passed.

#### 1.4.5 Shipment to U. S. Army Fuel and Lubes Research Laboratory

Fifty gallons of Alamac emulsion were prepared February 28, 1967, and sent March 15, 1967, to the U. S. Army Fuels and Lubricants Research Laboratory in San Antonio, Texas.

#### 1.4.6 Shipment to AvSER

One hundred and fifty gallons of emulsion were prepared during the period of March 16, 1967 through March 20, 1967 and were shipped March 20, 1967, to AvSER, Phoenix, Arizona.

The standard 18-minute method of preparation was used. An external phase of 3.00 volume % was used with JP-4 from the National Refining Company.

Periodic yield stress determinations ranged from 2400 to 2800 dynes/cm<sup>2</sup> immediately after emulsion preparation. Composite samples of emulsion from each mixing were kept for each drum of emulsion, and each passed the 7-day 135°F stability test.

## 2. Standard Procedure for Alamac Emulsion Manufacture

The emulsion consists of the external-phase concentrate (EPC), deionized water, and JP-4.

## 2.1 External-Phase Concentrate

	<u>Amt/Liter</u>	<u>Amt/Gal</u>	<u>Grams/Gal</u>	<u>Lb/Gal</u>	<u>Wt %</u>
Ethylene Glycol (sp.gr. 1.1155)	800.17 ml	3028.6 ml	3378.4	7.441	83.46
Glacial Acetic Acid (sp.gr. 1.0512)	33.01 ml	124.9 ml	131.3	0.289	3.24
Alamine H26D	141.57 g	535.79 g	535.8	<u>1.186</u>	<u>13.30</u>
				8.916	100.00

## 2.2 Raw Materials Costs

Exclusive of JP-4 and based on May 1967 quotations of Oil, Paint, and Drug Reporter.

<u>EPC</u>	<u>Wt %</u>	<u>\$/Lb</u>	<u>\$/100 Lb</u>
Ethylene Glycol	83.46 @	0.1350	11.27
Glacial Acetic Acid	3.24 @	0.0900	0.29
Alamine H26D	<u>13.30 @</u>	<u>0.3350</u>	<u>4.45</u>
	100.00		16.01

## 2.3 Alamac Emulsion

	<u>Vol %</u>	<u>Lb/100 Gal</u>	<u>Wt %</u>	<u>\$ EPC/100 Gal</u>
EPC	1.717*	15.309	2.43	2.45
Water	1.314*	10.965	1.74	-
JP-4	<u>97.0</u>	<u>602.244</u>	<u>95.83</u>	<u>-</u>
(sp.gr. 0.744)	100.0	628.518	100.00	2.45

\*Contraction to 3.0 Vol %.

## 2.4 Method of Manufacture

### 2.4.1 External-Phase Concentrate

To the proper volume of ethylene glycol, add the calculated volume of glacial acetic acid. Weigh out the proper amount

of Alamine, and warm until melted. Add the melt to the EG/acetic acid mixture with stirring (Lightnin' or other mixer), and stir until uniform.

#### 2.4.2 Emulsion

- 1) Transfer the required volume of EPC to the mixer, and add the deionized water. Stir (#2 speed of Hobart mixer) for 30 seconds.
- 2) Slowly add 2% of the total JP-4, stirring (#2) for 30 seconds. Maintain the o/w appearance of the emulsion, adding 10% of the total JP-4 over a period of 2 minutes.
- 3) Add 20% more of the JP-4 over a 4-minute period.
- 4) Add the balance of the JP-4 over a period of 3 minutes (#1 speed). Then stir at #2 speed for 8 minutes more.

#### 3. Reconstitution

Attempts were made to reconstitute a 50% broken Alamac emulsion with the Lightnin' mixer. However, only 90% of the emulsification was completed, at which point it became chunky and would not receive additional JP-4.

One-hundred-percent reconstitution was achieved when closed containers of broken emulsion were gently shaken by hand. This was accomplished with emulsions containing up to 80% JP-4 and emulsions which still contained a contaminant which was the original cause for separation.

Many subsequent reconstitution tests have been made with emulsions partially broken by thermal extremes, and all have been successful.

#### P. . . FUEL RECOVERY

##### 1. Recovery of JP-4 Fuel

A number of systems may be used in the recovery procedure, but because of logistics considerations, the obvious one is that operating with a minimum of attention, processing, and equipment. However, the recovered JP-4 is required to meet the MIL-T-5624G requirements. Should these requirements be

relaxed or specific exceptions be allowed, it is possible that a much simplified system might be developed.

Since the final candidate emulsion is that prepared with Alamac H26D emulsifier, only that will be discussed here. The recovery data developed for the Emcol emulsion are cited in Appendix V.

#### 1.1 Centrifugal Force

The Gyro Tester Centrifuge of the DeLaval Company operates at 10,000 g's, either as a test tube configuration or for continuous separation. Alamac emulsion tested in a test tube in this apparatus at 10,000 g's for 3 minutes failed to show any separation. The lack of separation is indicative of the high stability of this emulsion. When 50% water was added to the emulsion and the extended emulsion made uniform, again the same g-force and time of exposure failed to cause separation.

#### 1.2 Recovery by Shear

A 3400-rpm centrifugal pump (3-1/2-in. pump housing by 3/8-in. width of the four-bladed impeller), fitted with a 2-in.-diameter pipe inlet and flow control valve, was fitted for either a once-through or a loop arrangement for repeated passage. The pump was started, and after a few minutes the outlet valve was opened enough to start a slow flow. Both liquid JP-4 and unbroken emulsion emerged from the outlet for the two emulsions tested. About 30% of the Emcol CS-136 emulsion and 50% of the Alamac H26D emulsion were broken down in this once-through process. The test was repeated more precisely on a per pass basis to determine the relative breakdown for the Alamac emulsion:

<u>No. of Passes</u>	<u>% Free JP-4</u>
1	0
60	20
300	50

#### 1.3 Recovery by Shear-Chemical Treatment

The Alamac H26D emulsion was circulated for about 15 minutes at full speed, after which time it appeared that no more emulsion would be broken down. About 50% of the emulsion was recovered as JP-4 liquid. To this system of 50% broken

emulsion, about 0.1% dry aluminum sulfate was added. After only about a minute, the entire emulsion was broken.

In another test, the loop was filled with Alamac emulsion and a 1% quantity of ammonium hydroxide was added at the time the pump was started. The entire emulsion (500 ml) broke down almost immediately, and the external phase was dispersed uniformly throughout the JP-4 in very small droplets. For this reason, it required much more time for the external phase to settle than it did with gentle agitation.

From these data, it appears that shear alone will not result in complete recovery except by excessive recycling. Conversely, the Alamac emulsion will not be broken down entirely, at least by this system.

#### 1.4 Preferential Wetting

The emulsion, completely broken by the shear-ammonium hydroxide treatment, was cloudy in appearance and obviously required some method for separation of the external phase from the fuel.

A Whatman No. 42 filter paper was wetted with JP-4, and a partial vacuum filtration was attempted. However, both the water and the JP-4 went through the filter unseparated.

The broken emulsion was then filtered through 0.45-micron and 0.80-micron Millipore filters which had been JP-4 wetted. The unseparated emulsion came through the 0.80 filter; however, only JP-4 appeared to come through the 0.45 filter, at a painfully slow rate.

Another filtering medium tried was glass wool packed in a glass column. The glass column had a side tube near its bottom through which a partial vacuum was applied. It was hoped that the JP-4-wetted glass wool would coalesce the water and separate it while the JP-4 passed through the side tube, but no separation occurred.

This separation method failed to provide the necessary external phase removal.

#### 1.5 Recovery by Heat

Storage tests had shown that, at best, only incomplete separation of the emulsion occurred at 160°F, indicating that a considerably higher temperature would be required for complete separation. Since JP-4 contains considerable



low-boiling hydrocarbon (the Reid vapor pressure at 100°F showing that emulsion prepared at ambient conditions was reduced from an initial 3.15 psi to 2.53), this method appeared neither economical nor particularly safe (if higher temperatures were required) and certainly not an appropriate field separation method.

#### 1.6 Recovery by Chemical Demulsification

Initial work on the Alamac H26D emulsion showed that 1 vol % of concentrated (28%) ammonium hydroxide would instantaneously break the emulsion with gentle stirring. The external phase settled to the bottom in several minutes and left a clear JP-4 which did not require centrifuging. If the ammonium hydroxide was added without stirring, about 75% of the JP-4 emerged clear in about 10 seconds. The ammonium hydroxide neutralizes the acetic acid in the acetate, freeing the tallow amine.

Addition of 0.3% anhydrous sodium carbonate also broke the emulsion. This required considerable stirring and several hours for the external phase to settle out before a clear JP-4 was produced.

The amine was believed to be dissolved either in the fuel or in the freed external phase. However, a residue obtained during evaporation of the recovered fuel led to the development of a test to determine the percentage of amine in the recovered fuel. UOP Laboratory Test Method for Petroleum and Its Products #313-58 (p.355) was employed in titration of nitrogen bases. Samples of standard fuel and fuel doped with ~0.1% Alamac were titrated to standardize the test. Ten-ml aliquots of sample were titrated with 0.02N HClO<sub>4</sub> in the presence of 50 ml of glacial acetic acid. The standard fuel yielded no titratable nitrogen, but the doped fuel required a titration of 1.35 ml of 0.02N HClO<sub>4</sub>.

Because the test method might detect the ammonium hydroxide used to break the emulsion as amine, tests were made to examine this factor. The tests showed conclusively that ammonium hydroxide did not interfere, and that all the Alamac used was recovered in the fuel phase. Consequently, a method for removal of the tallow amine from the fuel was required.

##### 1.6.1 Preliminary Amine Removal Tests

A portion of extremely fine attapulgus clay was placed in a filter tube and broken emulsion was percolated through it. The fineness of the clay required suction to pull the fuel through the column. Percolated fuel and fuel allowed to

stand in the clay were analyzed, and it was found that 97% and 88% of the Alamac were removed, respectively. Two samples of coarser clays were obtained and gave these results:

<u>Attapulugus Clay</u>	<u>Results</u>
#1 50-80 RVM gravity fed - 60 ml/min	<0.0007 wt/vol % Alamac
#2 100-200 A, LVM gravity fed - 5 ml/min	<0.0007 wt/vol % Alamac
As recovered, untreated fuel	<0.346 wt/vol % Alamac

An additional 1400 ml of broken emulsion was filtered through a 100-ml volume of #1 (50-80 RVM) and collected in 100-ml volumes for Alamac analysis.

<u>Broken Emulsion</u>	<u>Amine, Wt/Vol %</u>	<u>% Alamac Removal</u>
100 to 1000 ml	<0.0007	100
1200 ml	0.0013	99
1400 ml	0.041	88

These data show that at least a 10:1 ratio of fuel to clay may be used without amine breakthrough.

#### 1.6.2 Final Removal Tests

A column partially filled with 3 liters of 60/90 RVM clay was set up, and 10 gallons (37 liters) of broken emulsion were filtered at a rate of 150 ml/min. All Alamac was removed, and the recovered fuel was used for determination of conformance to MIL-T-5624G requirements.

Column characteristics were the following: Diameter - 6.5 cm; height of clay column - 90.5 cm; volume of clay - 3 liters; weight of clay per liter - 454 grams.

#### 1.6.3 From Emcol Emulsion

A sample of broken and centrifuged Emcol CS-136 emulsion was filtered through the 50-80 RVM clay and submitted with other samples for ash analysis.

## 2. Ash in Emulsions and Recovered JP-4

Ash values for the emulsions and recovered JP-4 were determined by evaporating several charges (350-ml total in 50-ml aliquots) of the fuel in a platinum crucible at a low temperature. Any tar remaining was burned off prior to ignition at 1600°F for 1 hour in a muffle furnace (Table XXVII).

TABLE XXVII. EMULSION ASH			
	Weight Used (grams)	% Ash	Remarks
<u>Emulsion</u>			
Alamac H26D	204	0.0013	Beige residue
Emcol CS-136	212	0.0008	Glassy residue
Emcol CS-136 (repeat)	192	0.0011	" "
<u>Recovered Fuel</u>			
JP-4	258	0.00016	
Recovered JP-4 Alamac	259	0.0003	
Recovered JP-4 Emcol CS-136	184	0.0116	White ash plus blue-black ash
*Recovered JP-4 Emcol CS-136	50	0.0021	
*Filtered through 50-80 RVM attapulugus clay.			

Emission analyses of these ashes are shown in Table XXVIII.

The ash from the final Alamac removal tests (10 gal) was determined and the ash composition identified:

JP-4 as received	0.00016% ash
Recovered JP-4-Alamac	0.000135% ash

Qualitative emission test of Alamac JP-4 ash

Major - Si, Al  
Trace - Cu

TABLE XXVIII. ASH QUALITATIVE EMISSION ANALYSIS		
Sample	Major Constituents	Minor Constituents
Alamac Emulsion	Na,Ca	Si,Mg,Al,Fe
Emcol CS-136 Emulsion	Fe,Si,Al	Na,Pb
Broken Emcol CS-136		
White ash	Al	P
Blue-black ash	Al	
Recovered Emcol CS-136 (centrifuged & filtered)	Al	P (high trace Na,Zr)

### 3. Recovered JP-4 Quality Conformance

The JP-4 recovered from the large-scale preparation of Alamac emulsion (200-gal lot to Falcon Research and Development Co.) was tested in accordance with qualification requirements of MIL-T-5624G side-by-side with the JP-4 (En-Ar-Co Batch 29) from which the emulsion was made. The JP-4 was recovered by the ammonium hydroxide-attapulgite filtration procedure described above.

In general, the recovered JP-4 was at least equal to, if not superior to, the JP-4 as received. As might be expected, the IBP (initial boiling point), fuel evaporated, and gravity are different from the "as received" JP-4 due to loss of highly volatile low ends. Other slight variations occur, but none is of real importance.

It should be recognized that the attapulgite filtration will remove the corrosion inhibitor, antioxidant, metal deactivator, and probably the anti-icing additive.

The MIL-T-5624G requirements conformance is given in Table XXIX.

#### 3.1 Emulsifier in JP-4 from Emulsion Separated by Nonchemical Means

Closed jars of Alamac emulsion were subjected to 16 hours at -60°F and then an additional 2 hours at -70°F. The separated JP-4 was then decanted from the emulsion and checked for

TABLE XXIX. JP-4 RECOVERED FROM ALAMAC EMULSION AND CONFORMANCE TO MIL-T-5624G REQUIREMENTS				
Test	JP-4 Requirement	Control JP-4 National EN-AR-CO	Recovered Alamac Emulsion National EN-AR-CO	Method; Laboratory
Distillation	•	-	-	ASTM D 86; Phoenix
IBP	•	130°F	138°F	
Fuel Evaporated	•	187°F	194°F	
10%	•	209°F	214°F	
20%	290°F	263°F	270°F	
50%	370°F	351°F	353°F	
90%	470°F			
End Point, max	•	420°F	418°F	
% Evaporated, 400°	•	96.5%	96.0%	
Vol % Residue, max	1.5 vol %	1.0%	1.0%	
% Loss, max	1.5 vol %	0.5%	0.5%	
Gravity, °API	45.0 min 57.0 max	58.7	57.9	ASTM D 287; MRC
Specific Gravity	0.802 max 0.751 min	0.744	0.747	
Existent Gum	7 mg/100 ml max	0.0	0.0	ASTM D 381; Phoenix
Total Potential Residue, 16 hr	14 mg/100 ml max	0.0	0.8 (total soluble)	ASTM D 873; Phoenix
Sulfur, Total	0.4 wt % max	0.12%	0.05%	ASTM D 1266; Phoenix
Mercaptan, Sulfur	0.001 wt % max	<0.0001%	<0.0001%	ASTM D 1323; MRC
Reid Vapor Pressure, 100°F	2.0 psi min 3.0 psi max	3.15	2.50	ASTM D 323; MRC
Freezing Point	-72°F max	<-80°F	<-80°F	ASTM D 2386; MRC
Heat of Combustion, Net	18,400 Btu/Lb min	18,788	18,788	ASTM D 240; MRC
Aromatics	25 vol % max	7%	7%	ASTM D 1319; Phoenix
Olefins	5.0 vol % max	1%	1%	ASTM D 1319; Phoenix
Luminometer No.	60.0 min	85.5	83.7	P & W
Copper Strip Corrosion, 212°F	No. 1, max	1-A (slight tarnish)	1-A (slight tarnish)	ASTM D 130; Phoenix
Water Separator Index	85, min	99.7	99.5	FTM 791-3256; Nitro
Water Reaction, Interface Rating	Lt	Rating 1	Rating 1	FTM 791-3251; MRC
Thermal Stability Coker @ 300/400°F		No's 1-4, 1's	1 et seq, 1's	
Tube Rating	<3			
Hg ΔP	43"	0.08	1.0	
Filter Rating		71	70	
Particulate Matter	4 mg/gal max origin; 8 mg/gal max destination	Less than 4 mg/gal	Less than 4 mg/gal	ASTM D 2276; MRC
Fuel System Icing Inhibitor	0.15 vol % max 0.10 vol % min			
% Ash	-	0.00016%	0.000135% Major-Si, Al Trace-Cu	
*To be reported				

Alamine H26D. The JP-4 was found to contain 0.014 wt/vol % Alamine H26D, or only 4% of the amount present in the emulsion. The other 96% of the surfactant along with the water and glycol was retained in the emulsion.

#### 4. Corrosion by Recovered JP-4

Strips of various metals were half-immersed in both "as received" JP-4 and JP-4 recovered from the Alamac emulsion (clay-filtered). The metal strips were examined after 7 days at 77°F, and again after 7 days at 140°F. The results show (Table XXX) that recovered JP-4 was equal to or less corrosive than "as received" JP-4.

TABLE XXX. EFFECT OF JP-4 AND RECOVERED JP-4 ON VARIOUS METALS (HALF-IMMERSED)				
Metal	7 Days at 77°F		7 Additional Days at 140°F	
	Standard	Recovered	Standard	Recovered
Bare 2024	0	0	0	0
Clad 2024	0	0	0	0
Anodized Bare 2024	0	0	0	0
Bare 7075	0	0	0	0
Clad 7075	0	0	0	0
Bare 7079	0	0	0	0
Bare 6061-T6	0	0	0	0
Steel 4340	0	0	0	0
Magnesium Type III	0	0	0	0
Brass I	Small brown stains below surface		General brown stain below on both sides	Brown stain on one side only
Titanium	0	0	0	0
Hot Rolled Steel	Stain at interface		Medium general rust below surface	Light general rust below surface

## CONCLUSIONS

Of 69 emulsifiers subjected to preliminary screening tests, two types appeared most effective. These were a phosphorous-containing emulsifier (Emcol CS-136) comprising a combined nonionic and anionic type, and a mildly cationic (approaching an amphoteric) type product (Alamac H26D). The preparation of Emcol emulsion proved to be thermally (low-temperature) sensitive, leaving only the Alamac candidate.

This emulsion, designated Alamac H26D, successfully meets the contract requirements. It has a stress yield value of  $\sim 1300$  dynes/cm<sup>2</sup> and does not flow readily through a 2-inch length of 1/2-inch ID tubing. The emulsion is thermally stable (7 days) at -40° and 160°F. Acceleration of gravity up to 10,000 g and at levels of 500 g for 30 minutes, or 150 g for 1 millisecond, has no effect upon the emulsion. "Slosh" tests and vibration at  $0.4 \pm 0.1$  g for 24 hours at specified cycling conditions had no effect on the Alamac product.

This emulsion had an average gross heat of combustion (Btu per pound) of 19,426 vs JP-4 at 20,141. Lubricity tests (Shell 4-ball) on comparable bases showed JP-4 with a coefficient of friction and wear scar diameter, respectively, of 0.334 and 0.0849 vs Alamac emulsion at 0.224 and 0.0351. Electrical conductivity of the emulsion was 4.4-million mho/cm higher than JP-4, while static electrical charge buildup for the emulsion was negligible vs a negative  $8 \times 10^{-12}$  amps for JP-4.

Ratio of evaporation losses of JP-4 to Alamac emulsion after 6 hours at -20°F was 2:1; at 77°F, 9:1; and at 135°F, 18:1. Reid vapor pressure of the emulsion (100°F) was 2.55 psi vs 3.15 psi for JP-4. Recovered JP-4 was 2.53 psi, indicating that the lower value for the emulsion was due to volatile losses during handling.

Flame propagation tests showed JP-4 as being 87 times faster than Alamac emulsion, while the dynamic burning test showed that JP-4 spread over an area about 6.6 times greater than the emulsion. Flash point tests were JP-4 at 77°F and the Alamac emulsion at 137°F. Using the same Cleveland open cup equipment at 77°F, JP-4 flamed at once, but only after 16 minutes was the Alamac emulsion ignited. Once ignited, the emulsion burned for the same length of time as JP-4. Explosivity tests showed that the 50% lower explosive limit (LEL) of JP-4 was achieved in 11 minutes vs 55 minutes for



the Alamac emulsion, and that greater than 100 minutes was required for it to achieve the 100% LEL vs 22 minutes for JP-4.

The emulsion can be pumped readily, but it does not flow well into the pump inlet, resulting in pump cavitation.

Alamac emulsion caused negligible corrosion and has essentially no greater effect on fuel system components than JP-4. These findings were verified on the Allison T-63 fuel system.

The emulsion has the property of not sticking to metals, elastomers, or plastic surfaces.

Alamac emulsion partially broken by extremes of temperature or shear is rather easily reconstituted by mild mixing.

Recovery of JP-4 is rapidly and effectively achieved by adding 1 vol % ammonium hydroxide (28%), and the retained amine is removed by a single pass through an attapulgate clay bed. The recovered JP-4 meets essentially all the MIL-T-5624G requirements.

Table XXXI summarizes the test results data.

TABLE XXXI. SUMMARY OF TEST RESULTS FOR ALAMAC H26D EMULSION			
Property		Value or Comparison with JP-4	
<u>Thermal Stability, °F</u>			
-65		Broken	
-40		Stable	
77		Stable	
135		Stable >90 days	
160		6 days	
<u>Freeze-Thaw Stability</u>			
10 Cycles (77°F to -20°F)		Stable	
<u>Gravity (g) Loads</u>			
150 - 0.001 sec (impact)		Stable	
500 - 30 minutes		Stable	
10,000 - 3 minutes		Stable	
<u>Vibration</u>			
0.4 ± 0.1 g - 24 hours, cycled @ 5-32 cps		Stable	
"Slosh" - 240 cpm		Stable	
<u>Viscosity</u>			
Brookfield (#7 Spindle @ 2 rpm)		90,000 cps	
Yield Value - at once @ 77°F	2,100 dynes/cm <sup>2</sup>		
7 days @ 77°F	1,400 dynes/cm <sup>2</sup>		
-20°F	12,100 dynes/cm <sup>2</sup>		
<u>Vapor Pressure</u>		<u>Alamac</u>	<u>JP-4</u>
Reid - 100°F - psi		2.55	3.15 2.53*
*Recovered JP-4			
<u>Rate of Evaporation -</u>			
<u>% Loss - 6 Hrs</u>			
-20°F		1.7	10.1
77°F		5.5	47.0
135°F		40.5	71.0

TABLE XXXI - Continued		
Property	Value or Comparison with JP-4	
<u>Effect of Shear on Evaporation</u>	<u>Alamac</u>	<u>JP-4</u>
5 hrs recirculation	-4.2%	-
<u>Flammability</u>		
Flash - Cleveland Open Cup	137°F	77°F
Time Lapse - Cleveland Open Cup - Minutes	15	0
Explosivity - Minutes to JP-4 LEL	>100	21
Trough - Propagation - 10 ft	175 sec	2 sec
Dynamic Burning -		
Avg diameter of fireball for 3-oz fluid	2.5 ft	7.2 ft
Avg cross-sectional area - ft <sup>2</sup>	6.6	38.4
<u>Btu/Lb</u> (gross heat of combustion)	19,426	20,141
<u>Compatibility</u>		
Elastomers	Equal to JP-4	
Coatings - polyurethane	Slight degradation	
Buna N	Much degradation	
Groove Sealant	Much degradation	
Metals - single-panel couples	Very slight most metals Those with brass appreciable	
Allison Bench Tests	Negligible effect	
	<u>Alamac</u>	<u>JP-4</u>
<u>Lubricity-Coefficient of Friction</u>	0.224	0.334
<u>Effect of Static Charge</u>		
Electrical Conductivity, mho/cm	$4.1 \times 10^{-8}$	$8.5 \times 10^{-14}$
Static Buildup, amps $\times 10^{-12}$	0	-2.6 to -8.5
Static Charge on Stability	None	-

TABLE XXXI - Continued		
Property	Value or Comparison with JP-4	
<u>Microbial Growth Support</u>	Equal to JP-4	
<u>Reconstitution</u>	Can be reconstituted	
<u>JP-4 Recovery</u>	Rapid by chemical means	
<u>Recovered JP-4</u>	Meets most requirements	
	<u>Alamac</u>	<u>JP-4</u>
<u>Ash - %</u>	0.0013	0.00016
<u>Recovered JP-4 - %</u>	0.000135	
<u>Composition</u>	Some sodium, calcium (see discussion)	

## RECOMMENDATIONS

For a program where a product is to be developed to meet certain specifications within a given time period, it is necessary that potentially pertinent but not imperatively pressing problems be bypassed. Having shown the practicality and applicability of the product, the next phase for production purposes is a "polishing" operation, in which product improvement is attained and production parameters are defined.

### 1. Physical Properties (Emulsion)

Determination of the following properties will further define emulsion characteristics to provide leads toward usage or an improved product:

- Heat transfer coefficient
- Thermal expansion
- Vacuum expansion
- Globule size
- Viscosity vs aging
- Agitation after aging vs viscosity
- Wetting (critical surface tension)
- Splash profile vs viscosity
- Correlation between viscosity and pumpability at various temperature levels

### 2. General Improvements

- Inhibit separation with a coupling agent
- Improve microbial resistance
- Reduce corrosion and/or component attack
- Decrease vapor pressure by improved emulsification
- Improve pumpability (at normal and low temperatures)
- With improved pumpability, maintain minimized dynamic burning and splash profile

### 3. Optimization of Ingredients and Formula

- Optimize emulsifier combination or homolog
- Optimize emulsifier ratio (if mixture used)
- Minimize external phase

#### 4. Quality Control

Determine allowable variance in ingredients  
Establish control tests for raw materials and product

#### 5. Packaging

Minimize package corrosion by inhibitor usage or  
package coating  
Perform scaled-up temperature, transportation, and  
storage time tests

#### 6. Production

Develop satisfactory large-scale manufacturing system  
Develop simplified on-site continuous-flow production  
system

The foregoing program is best subdivided into two portions:  
(1) everything cited except the continuous production system,  
and (2) the development of the continuous production system.

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## APPENDIX I. PHASE I

### A. LITERATURE SURVEY AND METHOD OF EMULSIFIER SELECTION

The several objectives of this survey are to identify available emulsifiers and continuous-phase materials, and to develop and apply a method of selection based upon recent techniques in order to minimize the number of emulsifiers and continuous-phase materials to be tested.

#### 1. Summary

Presented is a review of the pertinent literature concerned with high-internal-phase JP-4 emulsions. This review indicates that these emulsions represent a relatively new technology which has as yet received comparatively little attention.

Discussed are the emulsifiers to be tested, their chemical and use properties, initial candidates, and a method for their selection. External-phase and viscosity modifier component requirements are defined and candidates discussed.

Given are the initially proposed methods of emulsifier selection and screening based on the theory that emulsifier mixtures would be required. A revised and much simplified method for selection and screening is given, because single emulsifiers perform quite satisfactorily.

Several prime candidate emulsions will emerge, based upon the preliminary and secondary screening results. A selection will be made from these to provide the two types of emulsions best meeting the contract requirements. These will then be submitted to the extensive and more rigorous tests and procedures cited in the work statement.

#### 2. Literature Survey

The chemical and petroleum literature dating back to 1955 and available from Chemical Abstracts has been reviewed, using as key words: colloids, emulsions, fuels, gels, gelation, jet fuel, kerosene, and petroleum. Emulsifiers and surfactants used for emulsions of fuel, kerosene, jet fuel, or petroleum were revealed in these four areas. The literature is replete with references to surfactants and emulsions in general, but their specific application to this problem is not available except as indicated below.

## 2.1 Emulsions

It is customary to find that emulsions of the oil-in-water (o/w) type are the subject of much investigation when the general objective is to extend oil as far as possible with water. However, the opposite case is not common, where oil is almost totally the other constituent. Paucity of literature references confirms this, indicating that emulsions of hydrocarbons as high-internal-phase ratio systems are a technology of comparatively recent origin.

No attempt will be made at a critical review of the literature for kerosene (JP-4) or petroleum-based emulsions whose internal-phase values are less than 80%. The older literature generally indicates an inversion from o/w to w/o at about a 75% content of hydrocarbon. One of the earliest references to the preferred emulsions is that of Pickering<sup>5</sup>, who prepared compositions containing up to 99% oil. A recent reference<sup>6</sup> cites a 70/30 o/w emulsion of No. 6 fuel oil using sodium oleate formed *in situ*. Cellulose acetate or cellulosic (ethyl) esters as emulsifiers gave liquid fuel emulsions containing 15 to 25% water<sup>7</sup>. An article by Lissant<sup>8</sup>, though concerned with the geometry of high-internal-phase ratio emulsions, indicates that the interest in these systems is recent, and that stable emulsions with 98% internal phase are possible. On June 7-8, 1966, an Aircraft Fluids Fire Hazard Symposium was held at Fort Monroe, Va. Yaffee<sup>9</sup> reported extensively on this symposium, which was sponsored by the Cornell Guggenheim Aviation Safety Center in cooperation with the U. S. Army Aviation Materiel Laboratories. Gels and emulsions were discussed and their characteristics considered. Described by Brown<sup>10</sup> were one gel, FAA-1069-1, containing 1.5% N-coco- $\gamma$ -hydroxybutyramide, by Western Co., Dallas, Texas; and two emulsions, EF4-101 by Petrolite Corp. and JD-1 by Western Co. Various surfactant concentrations were used for fuel emulsion modifications in continental's T72 turboshaft engine tests. Other engine tests, it is indicated, either have been initiated or are in the planning stage. Other papers on emulsified<sup>11</sup> or gelled<sup>12</sup> fuels were presented. One particularly pertinent paper by Lissant<sup>11</sup>, in which the same emulsifier was used as that detailed in his paper<sup>8</sup> on high-internal-phase ratio emulsions, described the emulsion as EF4-101, containing 2.8 wt % of external phase. Its other properties apparently meet many of the present requirements.

## 2.2 Gels

Although gels (liquid in a solid) *per se* are not the subject of this contract, emulsions (liquid in a liquid) can have gel-like structures so far as general appearance is concerned. The contract requirements as to flow (or nonflow) are most nearly met by a gel or very viscous emulsion. A thixotropic composition might readily meet the flow requirements. Since viscosity modifiers (gel formers) are one of the means for arriving at stable, slow-flow systems, these are briefly reviewed. Beerbower and Philippoff<sup>12</sup> reviewed the history, chemistry, and rheology of gelled fuels. Rapid gelation<sup>13</sup> of jet fuel to reduce fire hazard in crashed aircraft was indicated as potentially feasible with the reaction product of toluene diisocyanate and a primary amine, provided that fuel tank structure permitted good mixing. Martin<sup>13</sup> investigated rapid methods of gelling aircraft fuels, using amines and diisocyanates, finding that they could give particulate, viscoelastic, and dilatant gels at rates as fast as 0.04 second. Certain of these gels reduced vaporization rates, contained fuel while burning, and retarded the burning rate. Such agents were effective at 2.5 to 4 wt % concentration. Another gel was formed using lauryl hydroxybutyramide<sup>14</sup>.

Other agents described for gelling high-energy fuel were poly(acrylic acid) homopolymer, which has an average molecular weight of 2-3 million<sup>15</sup>. Fuel gels were obtained with polystyrene or polyisobutene<sup>16</sup>. A combination of abietylamine and carbon disulfide<sup>17</sup> gelled jet fuel in a ratio of 6-4-100 by volume. Stable, elastic gels of motor fuel were obtained using tall oil soap with ethylene glycol monomethyl ether or diethylene glycol in the ratio of 40 soap to 10 solvent per liter of fuel<sup>18</sup>. Lanosterol added to hydrocarbons in 8% to 15% amounts gave solid gels<sup>19</sup>. Methyl or methylethyl carboxymethyl cellulose was more effective for o/w dispersions than sodium carboxymethyl cellulose<sup>20</sup>. Thixotropic forms of diesel or jet fuels with lowered flammability were claimed by adding 0.25 part of the sodium salts of oleic and stearic acid to 100 parts of fuel<sup>21</sup>.

## 2.3 Surfactants

Desirable or necessary properties of an emulsifier for this purpose are:

Insoluble, slightly soluble, or partially miscible with JP-4.

Soluble in the external phase.

Capable of forming a stable film about the JP-4 internal phase.

Increases the viscosity of the internal phase or possibly causes thixotropy of the system.

Nonflammable.

Aids in reducing JP-4 volatility.

Combustible at engine temperature.

If burned, should minimize engine deposits and be free from metals.

Capable of removal by metathesis or other physical or chemical means.

These potential requirements are essentially those necessary for emulsion formation and stability, to provide a decrease in flammability, to be separable if this approach is chosen, or to be combustible in the engine.

In choosing a surfactant or combination of surfactants which can be consumed in the engine, the following essential components should be controlling:

Metals - (possibly introduced as the cation) must be absent to prevent engine deposits and/or alloying with turbine blade alloy.

Silicon - Not necessarily corrosive but could cause engine deposit.

Sulfur - Could cause engine deposits and potentially corrosive.

Phosphorus - Same characteristics as sulfur.

Chlorine - Probably corrosive.

Nitrogen - No apparent problem.

The other atomic components of surfactants, i.e., C, H, and O, present no problems.

With the foregoing reservations in mind, the surfactants least likely to cause difficulty and most likely to prove generally effective are nonionics, and mildly to strongly cationic agents (e.g., amides, amines, quaternaries). Provided that the quantities used are low, anionics containing

sulfur or phosphorus may prove to be marginally useful, as would quaternaries containing chlorine. For recovery of JP-4 fuel from an anionic (or cationic) emulsion, the anionic or cationic antagonistic reaction may be used to cause separation of the external phase. Metathetic reaction is not feasible with nonionics; therefore, other physical means for separation will be required if these emulsifiers are chosen for the separable fuel product.

C, H, O, and N nonionics are based upon substituent hydrogen groups which are reactive with ethylene oxide (EO) or propylene oxide (PO) or their glycols. The reactive H group of -OH, -COOH, -NH, and -CONH<sub>2</sub> chemicals, for example, forms adducts of variable but controllable ethylene- or propylene-oxide content. Glycols instead of the oxides may be used for condensation, and either may be reacted with fatty alcohols, alkyl phenols, fatty acids, fatty amines, or fatty amides, as examples of the relatively more simple materials; or they may be propylene oxide block polymers modified and solubilized with added ethylene oxide. The adduct length in any case may be controlled during preparation, from a very few EO groups promoting lipophilic activity to long EO chain lengths with many potentially hydrogen bonding ether linkages promoting hydrophilic character. Good emulsifiers have been prepared using adducts with two to five EO groups, which are sulfated to give anionic character to the nonionic structure.

Nonionic surfactants possess one characteristic potentially quite applicable to this program: they exhibit reverse solubility when their cloud point temperature is exceeded. This means that they can be almost quantitatively removed from solution at a sufficiently high temperature. Provided that they exhibit this same phenomenon in the selected exterior phase, this may prove to be valuable in the recoverable fuel portion of this project.

A recent type of surfactant suitable to this program is that containing both nonionic and relatively weak anionic groups. These are described as complex phosphate esters.

Amphoteric surfactants are also potential emulsifiers, but because of their cost, they may prove to be less desirable than others.

Amines such as fatty acid derivatives are also potential surfactants and may be reacted easily with carboxy or other acids to yield suitable emulsifiers.

Anionic surfactants to be chosen will be free of sodium, potassium, or metal constituents, such as salts of sulfuric or phosphoric derivatives. Instead, these will be ammonium, amine, alkanolamine, or other salt-formers to replace sodium, to minimize corrosion and engine deposits, and yet to retain their emulsifying capabilities. Examples of these bases are alkylaryl sulfonates or the low EO sulfate products.

In any event, surfactants chosen will be those that are compatible with the external-phase component and which also impart a degree of viscosity to the emulsions formed. This means higher molecular weight products exemplified by the higher fatty acid EO adducts.

The literature is replete with references to literally thousands of surfactants. A very useful compendium of currently available industrial surfactants is McCutcheon's annual<sup>22</sup>. Entries of surfactants are complete with trade name, manufacturer, class and formula, use, form, concentration, and type. This literature survey will be concerned only with surfactants used to emulsify hydrocarbons and fuel oils, and mainly with systems of high internal hydrocarbon phase.

A mixture of polyether thioether glycols is cited for emulsifying hydrocarbons<sup>23</sup>. Also, ammonium oleate and stearate are discussed as hydrocarbon emulsifiers<sup>24</sup>.

Thrust augmentation compositions are cited which are composed of water, alcohol, hydrocarbon, and a mixture (55-45) of Tween 20 and Span 20<sup>25</sup>. Amine salts of dihexylsulfophthalate or of sulfated higher alcohol-ethylene oxide adducts are claimed as hydrocarbon fuel emulsifiers<sup>26</sup>. Water dispersions of hydrocarbon resins were obtained with a mixed emulsifier of Ethomeen S-12, dodecyltrimethylammonium chloride, and octylphenoxy poly(ethoxy)ethanol<sup>27</sup>. Armeen S used as an inhibitor in distillate fuel oils caused emulsification<sup>28</sup>.

### 2.3.1 Surfactant Selection

The following examples of surfactants and their chemical structures are those initially to be investigated, though others having potential application will also be selected.

#### 2.3.1.1 Amphoteric Surfactants

Armeen E -  $R(\text{coco})-\text{NH}-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$   
Armac T - Tallow amine acetate

#### 2.3.1.2 Nonionics

Cerasynt 303	- Hydroxyethyl stearamide
Amidox C5	- Ethoxylated (coco) alkylolamide
Cardene	- N,N-bis(hydroxyethyl) oleamide
Alrosol O	- Fatty alkylolamide condensate
Emerest 2642	- PEG 400 distearate
Alrodyne 315	- PEG fatty ester
Emulphor ON-870	- Poly EO (ethylene oxide) fatty alcohol
Brij 56	- Poly EO (10) cetyl ether
Brij 72	- Poly EO (2) stearyl ether
Span 60	- Sorbitan monostearate
Span 65	- Sorbitan tristearate
Tween 60	- Poly EO sorbitan monostearate
Tween 61	- " " "
Sterox AJ	- Poly EO tridecyl ether
Priminox R-5	- C <sub>12-14</sub> amine EO (5) condensate
Priminox T-5	- C <sub>18-22</sub> amine EO (15) condensate

#### 2.3.1.3 Nonionic-Anionic

Antara LF-200 - Free acid of complex organic phosphate ester.

#### 2.3.1.4 Cationic

Adogen 340 - Trihydrogenated tertiary tallow amine  
Armeen T - Primary tallow amine

#### 2.3.1.5 Anionic

LAS-99 - Dodecylbenzene sulfonic acid

#### 2.3.2 Hydrophile-Lipophile Balance (HLB) Concept

The character of the internal-phase constituent may sharply affect either the type of emulsion or the emulsifier used. The ratio of internal to external phase is likewise important, as it is affected by both the external-phase constitution and the emulsifier. In this case, obvious interest is solely in high-internal-phase ratio emulsions of the o/w type. Deviations from the usual emulsions which generally contain water as the external phase make it necessary to have freeze-stable emulsions and a material which can lower the JP-4 vaporization rate.

A very important factor in emulsion technology is selection of the emulsifier. If there have been 10,000 surfactants synthesized, the chances are very good that all of them have been tested at one time or another as an emulsifier. Needed, therefore, is some systematic approach to emulsifier selec-



tion capable of reducing the otherwise laborious testing, not only of single emulsifiers but also of combinations of them.

A considerable amount of previous experience with emulsifiers for agricultural emulsions, using petroleum distillate solutions of the active insecticidal or herbicidal agent, indicated that optimum results were obtained with mixtures of anionic and nonionic emulsifiers.

Griffin<sup>29</sup> devised the HLB method which has been used relatively effectively for some time. One difficulty with its use is that either precise analytical data are needed to arrive at the numerical HLB value, or else a long and laborious experimental procedure is involved. As a consequence, several other approaches to arrive at either HLB or equivalent values have been attempted.

In one example<sup>30</sup> of an attempt to arrive at HLB values, emulsions were prepared and the HLB values determined by the inversion preparation technique. Griffin<sup>31</sup> developed an arbitrary technique showing ranges of HLB based upon water solubility:

<u>Behavior When Added to Water</u>	<u>HLB Range</u>
No dispersibility	1-4
Poor dispersion	3-6
Milky dispersion after vigorous agitation	6-8
Stable milky dispersion (upper end almost translucent)	8-10
From translucent to clear dispersion	10-13
Clear solution	13+

Where HLB literature values exist<sup>32</sup>, a short correlation of these with values obtained by another technique which has been used in evaluating ethylene oxide-based nonionic surfactants described by Greenwald *et al.*<sup>33</sup> is planned. This procedure consists of water titration of a dioxane-benzene solution of oil or surfactant to a cloud end point to give values related to HLB. While such values are not necessarily identical for all surfactants, this method permits a clearer

and simpler definition than the solubility technique or the calculation of HLB values from analytical or more tedious procedure. However, it is likely that any of these methods will be used as occasion demands.

The literature indicates that an HLB value of about 12.5 is a near optimum for emulsions of hydrocarbons of the nature of JP-4. Since HLB or a value correlatable with it seems to be the more direct approach, surfactants or surfactant combinations of HLB 12.5 (or equivalent) will initially be tested. A few of lower value will be included to verify the selection.

#### 2.4 External Phase

Properties of the external phase which would seem controlling in this project are as follows:

- Must reduce JP-4 volatility.

- Nonflammable.

- Combustible at engine temperature.

- Insoluble or, at most, very slightly miscible with JP-4.

- Have a low freeze point or be a freeze-thaw stabilizer.

- Capable of being separated from JP-4 emulsion by chemical or physical means.

If water possessed all the foregoing requirements, it would be an ideal material; however, it freezes relatively readily. To approach water's insolubility in JP-4, a material must be selected which has one or more hydroxyl or ether linkages without a large lipophile component, or must at least be strongly hydrophile.

The glycols, with ethylene glycol (EG) being the simplest example, closely approach the required characteristics. Also potentially useful are the polyglycols, propylene glycol(s), lower glycol ester, glycerin, ethoxy or methoxy triglycol, and even the liquid EO adducts. Methyl cello-solve, the chief constituent of the fuel anti-icing additive and itself an effective bactericide and fungicide, might prove useful in part, but is relatively expensive.

The hydrophile materials cited are also capable of hydrogen bonding. A search for materials of this nature indicated one other type as being potentially applicable: short chain alkylamides, such as formamide or acetamide.

Freeze and freeze-thaw stability may be prevented or enhanced by the foregoing agents, thus making water a potential portion of the emulsion for the desirable properties it may provide.

### 2.5 Viscosity Modifiers

It was expected that judicious selection of surfactant would result in emulsions of the desired viscosity characteristics, but in the event that this was not the case, viscosity modifiers would be investigated. Without regard to recovery of JP-4 fuel, these modifiers may be used preferably in the external or alternatively, the internal JP-4 phase. The desired characteristics for such agents are:

High capacity to modify viscosity.

Soluble in external phase and emulsifier or partially soluble or dispersible in JP-4.

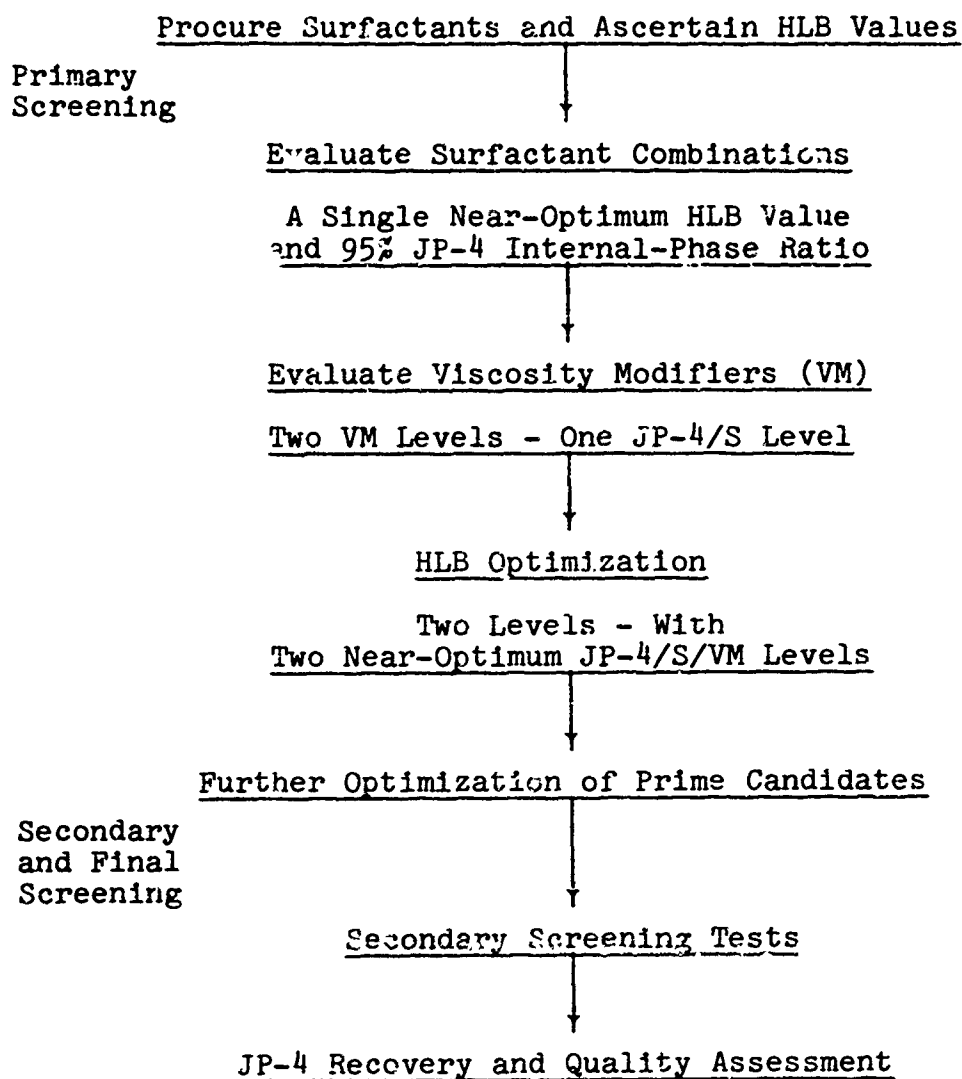
Combustible at engine temperatures and not cause engine deposits.

If such a modifier is necessary for the combustible formulation, it will be chosen with the necessary requirements in mind. Should the composition for recovery of JP-4 require a modifier, it too will be chosen based on these requirements but, additionally, will be susceptible to removal.

### 3. Method of Selection

The following program flow sheet and discussion outline more specifically our proposed attack on this project.

### 3.1 Proposed Program Flow Sheet



The objective of this work program is to minimize effort in order to arrive effectively at suitable product objectives.

### 3.2 Revised Program Flow Sheet

Experience with these emulsion systems reduced the actual program progression to the following:

Procure Surfactants and Ascertain HLB Values



Prepare 97% Internal-Phase JP-4 Emulsions



Primary Screening by Testing for  
Thermal Stability (-20°; 135°F)

500-g Stability  
Viscosity Measurement



Secondary Screening Tests



JP-4 Recovery and Quality Assessment

### 3.3 Proposed Preliminary Screening

The following program was designed to cover all possible variations which might be encountered in complying with the primary contract requirements. A subsequent section outlines the simplified system which was evolved.

#### 3.3.1 Experimental Design

Using a partial factorial design, the JP-4 phase (as volume %) will be tested against surfactant (S) (concentration in external phase) combinations at a single, near-optimum HLB value of 12.5.

<u>JP-4 (Vol %)</u>	<u>% Surfactant</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
95	I	+	II

The external fluid phase will comprise a 50/50 volume mixture of water/ethylene glycol. To 4 volumes of mixed external phase will be added 1 wt % surfactant. This completed external phase will be used to emulsify 95-vol % JP-4. Whether an internal phase greater than 95% is completely feasible will depend upon preliminary screening results. This means that another factorial experimental series based on the same surfactant combination would be prepared at 97% internal-phase levels, but at a surfactant level found satisfactory for the 95% system (increasing it if necessary).

### 3.3.2 Viscosity Modification

It appears likely that emulsion modifiers may be needed to meet the relatively high viscosity requirements. These will be tested under a partial factorial design similar to that used for the surfactant system. In this case, however, the highest feasible ratio of internal phase to total fluid will be used with the most effective surfactant combinations. In the following array, the 95 in 95/1 refers to 95-volume JP-4 with 1% surfactant emulsifier combination. Again, with satisfactory results at a 95% JP-4 internal ratio, the 97% level will be investigated.

<u>JP-4 Surfactant (S)</u>	<u>Viscosity Modifier (VM % in External Phase)</u>	
	<u>1</u>	<u>2</u>
95/1	I	X
or		
95/2	X	II

### 3.3.3 HLB Optimization

For preliminary screening, a single (according to the literature), near-optimum value of 12.5 will be used. Since indications are that initial viscosity values of high internal-phase emulsions decrease markedly on standing, it is likely that viscosity modifiers will be required. Following screening of these modifiers and selection of a suitable product, the HLB value for the system will be optimized.

<u>JP-4/S/VM</u>	<u>HLB</u>		
	<u>11</u>	<u>12.5</u>	<u>14</u>
95/1/2	I	X*	IV
95/2/1	II	X*	III

\*Already tested

The order of test initiation should indicate prime candidate systems so that the remainder of test systems can be disregarded.

### 3.4 Revised Preliminary Screening

#### 3.4.1 HLB Determination

Surfactants were chosen which experience indicated should prove applicable, and the HLB values either were used as supplied or were determined using the solubility concept. The main objective in using HLB values was to minimize the experimental work should combinations of surfactants prove to be the only approach. However, it now appears that the more effective emulsifiers are indeed those of HLB values of 12 or greater, and single surfactants meet this requirement best. A few surfactants of lower HLB were tested to verify this finding, and it is very likely that the high-internal-phase concentration has a strong effect on this selection.

#### 3.4.2 Emulsion Preparation

Since the emulsions are to contain not less than 97% internal JP-4 phase, the 3% balance of the formulation will consist of emulsifier, water, and glycol, or other fire and freeze depressant. The surfactant screening operation was established on the basis that 10% of the 3% balance be surfactant and that the fluid portion be equally divided between water and glycol (arbitrarily 0.3 wt % emulsifier, 1.37 vol % water, and 1.37 vol % ethylene glycol).

The emulsions are prepared in a standard manner, homogenizing first the external phase, then adding the JP-4 gradually. The emulsions thus prepared are ready for primary screening.

#### 3.4.3 Primary Screening Tests

Primary screening comprises tests easily made and which must be passed before secondary screening is initiated.

The first requisite is physical stability at -20°F and 135°F. Observations are made after 1 hour, after 24 hours, and after 7 days. If the 7-day test is passed, the retained sample is stored at 75° ± 2°F for 30 days.

The freshly prepared emulsion is subjected to a 500-g stability test for 30 minutes.

The viscosity of the emulsion is measured with a Brookfield RVF viscometer at 2, 4, 10, and 20 rpm to give a comparative measure of viscosity.

If the emulsion can pass the foregoing tests, it is then subjected to secondary screening procedures.

### 3.5 Secondary Screening Tests

Since emulsified fuel must be stored and transshipped, it is likely that JP-4 fuel drums may be used. Consequently, a strip cold-rolled mild steel is partially immersed in a capped 4-oz jar of the emulsion and stored 30 days at  $75^{\circ} \pm 2^{\circ}\text{F}$ . Lack of corrosion and continued emulsion stability are necessary.

Other tests in this category are rate of evaporation, rate of burning, ash content of burned emulsion, corrosion of other metals, compatibility with fuel system nonmetallic components, as well as other specific contract requirements. However, these latter tests are to be performed only on the compositions which survive the primary and early secondary tests. Obviously, simulated engine burning tests are a necessity.

### 3.6 JP-4 Recovery

Preferred compositions from preliminary and secondary screening will be tested to determine by what means the JP-4 satisfactorily may be recovered. The suggested recovery systems are chemical, thermal, shear, or combinations of these. The most effective will be determined, and JP-4 recovered by this means will be tested for compliance with the controlling military specification.

## B. WATER NUMBER OF EMULSIFIERS

The water titration of a dioxane-benzene solution of a surfactant to a dense cloud end point was used by Greenwald, *et al.*,<sup>33</sup> to determine a value related to the HLB of the surfactant.

This technique was applied to the measurement of water numbers of various surfactants of known HLB. Comparison of the experimentally found water numbers with the published HLB values shows that the water number serves as an indication of the HLB value. The correlation is readily obtained if the surfactants are grouped in families, i.e., poly(oxyethylene) sorbitan stearates, poly(oxyethylene) ethers, and



surfactants without ethylene oxide adducts. See Table XXXII and Figure 14. However, this procedure did not provide the full coverage of all surfactants and was time-consuming, and another method was sought to simplify HLB determination and to make it more broadly useful.

TABLE XXXII. WATER NUMBER OF EMULSIFIERS		
Surfactant	HLB	Water No.
Poly(EO)Sorbitan Stearates		
Tween 61	9.6	8.7
		8.9
		8.8
Tween 60	14.9	17.2
		17.3
Tween 80	15.0	15.5
		15.5
Tween 20	16.7	20.4
		19.7
Poly(EO)Ethers		
Brij 72	4.9	15.0
		16.4
Brij 56	12.9	38.1
		40.1
Brij 58	15.7	48.3
		47.1
No EO Adducts		
Span 65	2.1	2.4
		2.6
Atmul 84	3.8	3.8
		3.6
Span 60	4.7	6.3
		6.3
Span 40	6.7	8.7
		8.5

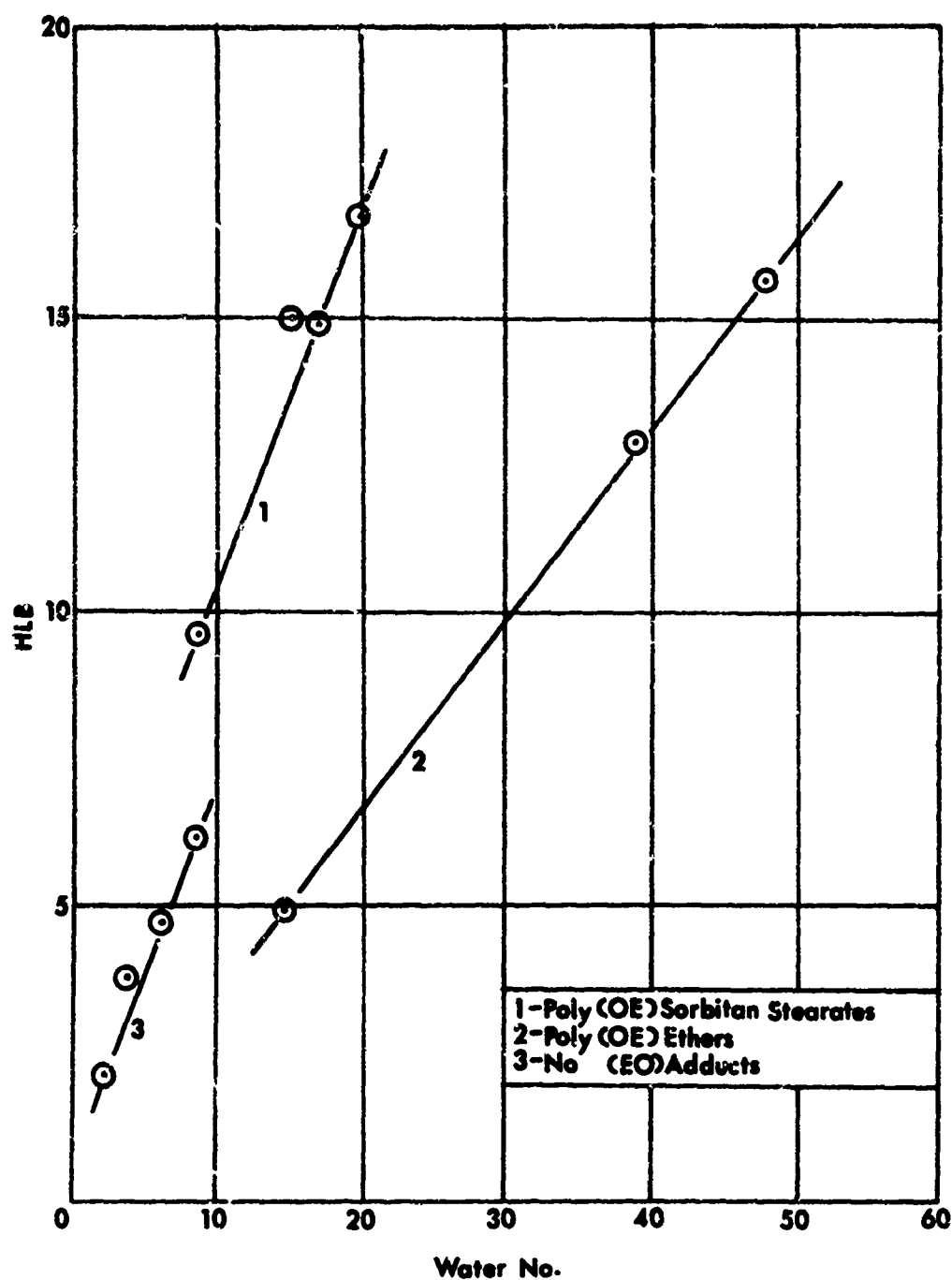


Figure 14. Correlation of HLB With Water Number.

C. PROCEDURE FOR 95% INTERNAL-PHASE COMPOSITIONS

Emulsions and gels were produced by dissolving or dispersing 5.0 grams of surfactant in a solution of 10 ml of water and 10 ml of ethylene glycol. While stirring slowly, 475 cc of JP-4 were added in small portions in a Hobart mixer, allowing for complete mixing before the addition of the next portion.

APPENDIX II. EMULSIFIER COMPOSITIONS

No.	Emulsifier	Chemical Constitution
41	Tween 20	Polyoxyethylene(20)sorbitan monolaurate
42	Emcol CS-141	Fatty alcohol phosphate ester with EO
43	Tween 60	Polyoxyethylene(60)sorbitan monostearate
44	As 43	
45	Antara LE-600	Free acid of complex organic phosphate ester
46	Emcol CS-136	TEA salt of nonylphenol(6)ethoxy phosphate ester
47	Brij 58	Polyoxyethylene(20)cetyl ether
48	N-Coco-γ-hydroxybutyramide	
49	Emcol CS-131	TEA salt of tridecyl alcohol phosphate diester with 6 EO
50	Emcol CS-140	" " " " - with 9-1/2 EO
51	Emcol CS-151	" " " " - with 12 EO
52	Acetamide	
53	See Table I	
54	Propionamide	
55	Armeen SZ (40%)	Alkali metal salt of N-coco amino butyric acid
56	Aromox DMCD (40%)	Dimethyl alkylamine oxide (cetyl?)
57	Aromox DMHTD (40%)	" " " (hydrogenated tallow?)
58	Ammonyx SO (30%)	Stearyl dimethyl amine oxide
59	Ammonyx LO (30%)	Lauryl dimethyl amine oxide
60	Ammonyx CO (30%)	Cetyl dimethyl amine oxide
61	Emcol CS-187	TEA salt of complex phosphate ester
62	See 61	
63	Armeen Z (55%)	Amphoteric coco amine crotonate
64	See Table I	
65	Formonyte 801	N-Alkyl trimethylene diamine
66	Duomeen C	N-Coco trimethylene diamine
67	Duomeen T	N-Tallow trimethylene diamine
68	Ethomid HT/15	Tallow ethylene oxide(15)amide
69	Ethomid HT/60	" " " (60) "

### APPENDIX III. RHEOLOGICAL MEASUREMENTS

The rheological experiments reported here were attempts at more precise measurement of rheological properties or development of a rapid control procedure. Also reported are the initial attempts to use the penetrometer to provide yield stress data.

#### A. INSTRON EXTRUSION RHEOMETER

Since the apparent viscosity values of JP-4 emulsions obtained on the Brookfield RVF were neither entirely satisfactory nor absolute, an attempt was made using the extrusion rheometer. However, the results were not significant due to the small forces needed to push these emulsions through an orifice at a constant piston travel rate.

The "CD" cell was set for the highest sensitivity to give the recorder a 4-lb full-scale reading, and the smallest orifice of 0.055-inch diameter was used.

The fastest load rate of 20 inches per minute was applied, and the only difference in loads between the thickest and thinnest emulsions was 0.02 lb. The Tween 60 emulsion required 0.08 lb and the Antara LE-600 emulsion required only 0.10 lb.

However, these loads are too small for the instrument to be significant, and they can hardly be distinguished from background recorder noise due to the high sensitivity and drag of the loading ram against the cylinder wall. The use of this principle in measuring apparent viscosity would require the "Pressure Viscometer," where a much smaller orifice is used and smaller pressures can be measured. Data are shown in Table XXXIII.

#### B. FALLING BALL METHOD

Needed for control purposes in emulsion preparation is a simple procedure which will differentiate satisfactorily between production lots to assure quality control. A recognized, absolute method to define this characteristic of emulsions also is desired.

This preliminary method is meant only for control purposes. The ball dimensions can be varied as necessary, and the test is reasonably reproducible.

TABLE XXXIII. VISCOSITY BY FALLING BALL - TRIPLICATE DETERMINATIONS			
Emulsion	Travel Time (Min)	Standard Deviation	Brookfield Viscosity (cps x 10 <sup>-3</sup> ) Spindle & Speed
0.3% Tween 60	0.08	0.00	65
0.4% Gafac RM 410 + TEA	0.10	0.01	70
0.4% LF-200 + TEA	0.11	0.01	
At once			0
1 day			110
2 weeks			85
0.3% Armeen SZ	2.03	0.06	
At once			190
2 weeks			70
0.4% LF-200 + TEA (1-day-old)	11.10	1.02	140
0.3% Alamac H26D	9.77	1.14	100
0.3% Emcol CS-136	(Ball wouldn't move, even with shaking)		100
0.4% Antara LE-600	(Ball wouldn't move, even with shaking)		170

The time was measured for a 7/8-in. OD steel ball to travel through 5 inches of emulsion under the influence of gravity. A glass cylinder 5-7/8 in. high and 1-1/2 in. in diameter was used as the container.

The steel ball was placed in the bottom of the glass cylinder, which was then packed with the emulsion to be tested. Aluminum foil was stretched across the cylinder top after the emulsion was leveled off. The cylinder was then turned upside down, and the time it took the ball to reach the bottom was recorded. The test was repeated in triplicate for each emulsion, and the standard deviation of the results was calculated.

A viscosity was also run on emulsion from each of the test batches using the No. 7 spindle, 2-rpm speed of the Brookfield RVF viscometer.

Each emulsion used in the above tests was between 1 and 2 days old, except for the 2-week-old LF-200 emulsion deliberately run for comparison and the 2-week-old Armeen emulsion which had just passed the initial tests.

#### Steel Ball Data

Wt. of Ball	-	44.8 grams
Volume	-	5.75 ml
Density	-	7.8 grams/ml

A degree of differentiation between emulsions was apparent (Table XXXIII). In the cases where extremely rapid drop or none at all occurred, adjustment in ball dimensions and weight could be used whenever a prime candidate is selected. There is reasonable correlation between the falling ball and the Brookfield methods, though neither provides absolute values.

#### C. YIELD POINT (PENETROMETER)

In order to get a valid comparison of the relative rigidity of emulsions, a method was devised to determine their yield points. A full-scale cone from an ASTM Grease Penetrometer apparatus (D 217-65T) was attached to the crosshead of the Instron Universal Testing Machine. This cone was pushed through the emulsion at three different rates, and the resulting loads were continually charted. The motion was started with the tip of the cone just touching the level emulsion surface in a full 1000-ml Griffin beaker. As the cone penetrated the emulsion, the load steadily increased



and recorded a straight line on the chart. At the point where the maximum surface area of the cone had penetrated the emulsion, there was a decreasing change in the slope of the chart line, and the corresponding load at this point can be considered the yield load of the emulsion. Dividing this load by the surface area gives a yield point (grams/cm<sup>2</sup>). The cone travelled at speeds of 20 in./min, 2 in./min, and 0.2 in./min. Since the results were the same at the two lower speeds, they were used to calculate the yield points. Results for the various emulsions are shown in Table XXXIV.

TABLE XXXIV. VISCOSITY-YIELD STRENGTH AND CONE  
PENETROMETER SUPPORTING STRENGTH

Emulsion	Instron				Cone Penetrometer		
	Load in Grams		Yield Strength Dynes/cm <sup>2</sup>	Cone Penetration 0.1-mm Units	Supporting Strength Dynes/cm <sup>2</sup>		
	Different Travel Rates						
	20 in./min	0.2 in./min					
	2 in./min	156 in./min	3130	330	2300		
Emcol CS-136	185	157	156	3130	330	2300	
Antara LE-600	186	155	155	3110	349	2000	
Alamac H26D	143	116	115	2300	393	1400	
Antara LF-200	120	106	89	1780	-	-	

#### APPENDIX IV. LARGE-SCALE EMULSION MANUFACTURE

##### A. TOWER PAINT COMPANY TRIAL

Forty- and fifty-gallon batches of Emcol CS-136 emulsion were made at a local paint company using a 70-gallon-capacity mixer. This mixer was single action and consisted of a horizontal bar to which were attached two vertical-plane, half-moon-shaped metal bars, which started at each end and projected two-thirds of the length of the bar. Thus, the bars overlapped each other and tended to give a folding-over action to the emulsion. This bottom rotating bar covered nearly the entire area of the mixer. Preliminary tests showed that this mixer would produce an emulsion.

A 40-gallon batch was prepared first with the aid of an 8.2% premix. This amount of premix was chosen because it could be contained in a 5-gallon can and was sufficient material for good mixing. It required 80 minutes to add the JP-4 in about 2-gallon additions, and the emulsion formed easily. However, it never appeared as "fluffy" as the standard Hobart mixer emulsion, and a thin film of JP-4 remained between the container sides and the emulsion. A gallon sample was taken after 80 minutes and again after 15 minutes of additional mixing. The emulsion was poured into a 55-gallon drum. After 3 days at 75°F, there was 10% free JP-4 in the drum (Table XXXV, 46-31).

A 50-gallon batch was next prepared with the aid of a 6% premix. This time the JP-4 was added in smaller quantities (1/2 gallon) and required 2-1/2 hours. Mixing was continued; gallon samples were taken 3 hours 15 minutes later and, again, 40 minutes later. After another 1/2 hour of mixing, there was still a thin film of JP-4 along the sides; so, for another 1/2 hour of mixing, baffles were inserted into the tank for cross-mixing, and the emulsion was cycled out the bottom of the tank back into the top. This initially thickened the emulsion, but still left the film of JP-4 along the edges. The fourth and final gallon sample was taken, and the emulsion was scooped into a 55-gallon drum (rusty from previously contained JP-4, but free of loose rust). This emulsion also broke down in the drum as shown in Table XXXV (46-32), but was more stable than the 40-gallon batch.

It was observed that the first gallon sample of the 40-gallon batch could be reconstituted into an emulsion by gentle shaking of the jar. This emulsion was also unstable (Table XXXV, 46-35).

TABLE XXIV. MIXER EVALUATION

Surfactant No.	Surfactant Name	Wt. % Surf.	External Phase Vol. %		Preparation and Stability
			H <sub>2</sub> O	St. Glycol	
46-31	Emcol CS-136	0.3	1.37	1.37	40-gallon batch, 0.2% premix; Tower Paint Co.; Two 1-gallon samples taken 15 minutes apart (#1 and #2); emulsion stored in 55-gallon drum. Stability: #1 - 75°F: 3 days-10% JP-4; 7 days-20% JP-4; -20°F: 7 days-N.C.; 135°F: 7 days-5% JP-4. #2 - 75°F: 3 days-20% JP-4; 7 days-30% JP-4; -20°F: 7 days-N.C.; 135°F: 7 days-5% JP-4. 55-gal. drum - 75°F: 7 days-20% JP-4.
46-32	Emcol CS-136	0.3	1.37	1.37	50-gallon batch, 6.0% premix; Tower Paint Co.; gallon samples taken when finished (#1), 15 minutes later (#2), 40 additional minutes (#3), and 65 additional minutes with recirculation (#4). Emulsion stored in 55-gallon drum. Stability: #1 - 75°F: 7 days-1% JP-4; -20°F: 7 days-1% JP-4; 135°F: 7 days-syneresis #2 - 75°F: 7 days-1% JP-4; -20°F: 7 days-N.C.; 135°F: 7 days-syneresis #3 - 75°F: 7 days-1% JP-4; -20°F: 7 days-N.C.; 135°F: 7 days-syneresis #4 - 75°F: 7 days-syneresis; -20°F: 7 days-N.C.; 135°F: 7 days-N.C. 55-gal. drum - 75°F: 3 days-syneresis; 7 days-1% JP-4; 14 days-5% JP-4
46-33	Emcol CS-136	0.3	1.37	1.37	Hobart Mixer, 6400 cc batch, 10% premix, remaining JP-4 added in one slug, required 8 minutes - emulsion stable.
46-34	Emcol CS-136	0.3	1.37	1.37	46-31, #1 sample; reshaken by hand back into emulsion after 20% had broken. Stability: -20°F and 135°F - N.C.; 75°F gallon jar - 5% JP-4.
46-35	Emcol CS-136	0.3	1.37	1.37	46-31, #2 sample; reconstituted with Hobart mixer after 40% had broken. Stability: -20°F and 135°F - N.C.; 75°F gallon jar - 5% JP-4.
46-36	Emcol CS-136	0.3	1.37	1.37	Lightnin' mixer, Dispensator mixer, then Kitchen Aid mixer, 1500 cc batch. Stability: 75°F, 7 days - 1% JP-4.

It was observed under the microscope that the emulsion drop-lets of the reconstituted emulsion ranged from 3 to 100 microns and that those of the 40-gallon emulsion ranged from 3 to 40 microns, while a standard Hobart mixer emulsion ranged from only 3 to 10 microns.

Relative viscosities of the various gallon samples from the 40- and 50-gallon batches were determined with the modified cone penetrometer, and from the depth of penetration the yield stresses were calculated as shown in Table XXXVI.

TABLE XXXVI. YIELD STRESS VALUES FOR LARGE BATCHES								
Batch:	Hobart Mixer	40-Gallon			50-Gallon			
Sample:	Stable Emulsion	#1	#2	#1*	#1	#2	#3	#4
Penetration (avg of 3 in./mm)	330	342	330	306	340	338	340	326
Yield Stress (dynes/cm <sup>2</sup> )	2288	2061	2288	2820	2100	2140	2100	2360
*Shaken								

The above results show good correlation between samples from the same mix. However, the results of the penetrometer will apparently not fingerprint a stable emulsion when different methods of mixing are used.

#### B. RECONSTITUTION

When the #2 sample of the 40-gallon batch was about 40% broken, it was reconstituted into a finished emulsion with the Hobart Mixer. It appeared to be a normal, stable Hobart emulsion, but produced free JP-4 after 7 days at room temperature (Table XXXV, 46-35). This showed that even a good mixer will not reconstitute poorly made emulsion. This was demonstrated further when three different mixers were used in making an emulsion (Table XXXV, 46-35). The Lightning Mixer was used first until 80% of the JP-4 had been emulsified. At this point no more fuel would emulsify. The use of the Dispersator mixer only made the emulsified part

chunky, which was then shown to still be o/w by its dispersion in water. Finally, the Kitchen Aid mixer had to be used to make what appeared to be a normal emulsion. However, after 12 days at room temperature, it too began to separate free JP-4 fuel.

## APPENDIX V. JP-4 RECOVERY

### A. RECOVERY FROM EMCOL EMULSION

A significant portion of the contract requirements was the development of emulsions, one of which must be capable of being broken for JP-4 recovery. The body of the report shows the data developed for recovery from the Alamac H26D emulsion, since it proved to be most amenable both to recovery and use *per se* in the engine. This Appendix covers the data developed for recovery from the Emcol emulsion.

### B. SHEAR

Opposites are involved in the requirements for JP-4 emulsions, in that a high degree of stability is required and that one type of emulsion should be amenable to recovery of the fuel. Certainly the emulsion should be stable enough to be pumped, which means a degree of shear, though shear may be one significant means for breaking the emulsion.

In these preliminary tests, the objective was to estimate the ease and extent of emulsion breaking.

A Waring Blendor operated at 15,000 rpm (Stroboscope) was used, just covering the blades with the emulsion. These data are shown in Table XXXVII.

### C. PREFERENTIAL WETTING

A Selas filter (0.6-micron porcelain filter pore size) has been used successfully for low-internal-phase emulsion separation, and was used with several of the more effective emulsions. However, with these high-internal-phase emulsions, filter plugging occurred immediately and separation ceased.

In another attempt, a #42 Whatman filter was wetted with JP-4 and a vacuum filtration attempted. However, again the separation rate was very low, and some of the emulsion passed through the porous openings.

TABLE XXXVII. JP-4 RECOVERY BY SHEAR*			
No.	Emulsion	Time of Shear	Miscellaneous Results
		% Emulsion Broken	
39-1	Gafac RM 410	15 sec.	Unbroken; settled to the bottom.
39-1	Gafac RM 410	5 min.	JP-4 cloudy; a clear layer of grease on bottom would not pour.
45-3	0.4% Antara LE-600	5 min.	Except that which stuck to walls of blender.
45-6	0.3% Antara LE-600	15 sec.	" " "
45-6	0.3% Antara LE-600	5 min.	" " "
46-1	Emcol CS-136	5 min.	Not counting that stuck to walls.
40-2	Antara LF-200	5 min.	Clear JP-4; no visible film on bottom.
43-4	Tween 60	5 min.	Cloudy JP-4; layer of grease on bottom.
41-2	Tween 20	5 min.	Cloudy JP-4; layer of grease on bottom.
*Waring Blendor 15,000 rpm - Emulsion just covered all four blades.			
NOTE: When Waring Blendor was first started up, it tended simply to cut a hole in the gel. However, once the JP-4 appeared, it sloshed the rest of the emulsion enough that the blades eventually sheared all the emulsion.			



#### D. SHEAR AND PREFERENTIAL WETTING

The Waring Blendor was used to break the emulsion, and this then passed through a Millipore filter. The 0.8-micron filter was more satisfactory on straight fuel than the 0.45-micron filter.

An emulsion was broken in the Waring Blendor, and the separated JP-4 vacuum filtered through a 0.8-micron Millipore filter. The JP-4 filtered in a continuous stream, and the volume reduced only when unbroken pieces of emulsion clogged the filter. This approach has much to recommend it on a practical basis and will be investigated further.

#### E. CHEMICAL DEMULSIFICATION

Various hydrophile materials were added to the 0.3% Antara LE-600 emulsion (45-3) in a beaker with stirring, with the following results. About 60 ml of emulsion was used in each case.

##### 1. 85% o-Phosphoric Acid

0.4 gram was added and thinned the emulsion without noticeably breaking it. A total of 2 grams (by continually adding dropwise and stirring) broke about 80% of the emulsion.

##### 2. Aluminum Chloride (Anhydrous)

0.2 gram was added and even without stirring, it sank into the emulsion by its own weight, breaking the emulsion as it went. With stirring, about 70% of the emulsion was broken after a few minutes, and a brown precipitate had formed from reaction with the surfactant. A total of 0.4 gram completely broke the remaining emulsion in a short time, leaving a water layer on the bottom and a cloudy JP-4 phase.

##### 3. Aluminum Sulfate (Not Anhydrous)

0.4 gram broke about 40% of the emulsion slowly.

##### 4. Aluminum Acetate (Niacin)

0.4 gram had no effect.

5. Calcium Sulfate (Anhydrous)

0.4 gram had no effect.

6. Sodium Carbonate (Anhydrous)

0.4 gram broke about 98% of the emulsion very slowly.

7. Molecular Sieves (60-100 mesh) 5A and 3A

Neither had any effect.

The foregoing experiments showed the combination of dried aluminum sulfate with mixing action to be the most effective way to break the emulsion completely. When the stirring was stopped, most of the external phase sank to the bottom and cloudy JP-4 remained. Various attempts were made to clear the JP-4 fuel completely, as follows:

1/2-hour centrifuging at 100 g's - Clear JP-4.

Water coalescer cell (Federal Test Method 791) -  
No visual effect.

Six water coalescer cells in series - No effect.

Activated 14-30 mesh molecular sieve 4A - No effect.

Anhydrous  $\text{CaSO}_4$ , gravity filtration - No effect.

Activated  $\text{Al}_2\text{O}_3$  (80-200 mesh), gravity filtration -  
No effect.

Also tried was breaking the emulsion by adding the 0.3% aluminum sulfate to the emulsion after it had been dissolved in 10% water. It was hoped that the excess water would drag all the external phase to the bottom and leave clear JP-4. The JP-4 was still cloudy but did clear up after setting several days, which did not happen without the water.

Since the centrifuge appeared to be the only practical way of JP-4 clarification, a Gyro Tester Centrifuge was obtained from the DeLaval Company for experimental work. This centrifuge operates at 10,000 g's and can be operated as either a test tube or a continuous-process centrifuge. The results of the continuous-process centrifuge can then be used to prescribe a suitable large-capacity centrifuge.

The Gyro Tester was first used as a test tube centrifuge for the following trials (40 seconds required for full speed):

Unbroken Emcol Emulsion, 3 minutes to 10,000 g's -  
No separation.

Unbroken Alamac emulsion, 3 minutes to 10,000 g's -  
No separation.

50% water added to unbroken emulsions - No emulsion  
breakdown.

Broken Emcol emulsion at following times:

3 minutes to 10,000 g's - Clear JP-4  
40 seconds to 10,000 g's - Clear JP-4

The fact that the JP-4 had cleared by the time the centrifuge had reached top speed indicated that the continuous-process centrifuge could be successfully used.

The centrifuge was primed with water, and four 6.5-mm regulating screws were used to adjust the position of the interface between the water and the fuel. However, the JP-4 that emerged was cloudy, both when the cloudy JP-4 was fed slowly from a beaker and also when fed at a rate of 450 cc/min by a gear pump. Recycling the JP-4 twice by both "feeding" methods still did not clear the JP-4.

Three 4.5-mm regulating screws and one 5.5-mm regulating screw replaced the four 6.5-mm screws. The JP-4 emerged clear after only one pass through the centrifuge, both when fed from a beaker and through the gear pump.

## APPENDIX VI. MICROBIOLOGICAL DATA

### GROWTH AND SURVIVAL OF FUEL-ISOLATES IN JP-4 EMULSIONS AND NONEMULSIFIED FUEL SYSTEMS

Microorganisms of the genera *Pseudomonas* and *Hormodendrum* have been isolated from a variety of hydrocarbon systems<sup>34-40</sup>. Specific types in these genera grow abundantly in a mineral salts solution<sup>36</sup> with JP-4 jet fuel as the sole carbon source<sup>38</sup>. Microorganisms of other genera have also been isolated from jet fuel systems<sup>36,38</sup> and petroleum oil fields<sup>35,40</sup> but not all of them grew in a mineral salts solution with hydrocarbons as the sole carbon source.

This study was undertaken to determine the growth response of representative microorganisms isolated from fuel systems in mineral salts media, when JP-4 jet fuel was supplied in emulsified form as the sole carbon source. The growth response was compared with the response in a similar system containing nonemulsified JP-4 fuel.

#### A. MATERIALS AND METHODS

##### 1. Culture Media

Microbial growth was determined in both liquid and solid test systems. The test systems were composed of a mineral salts solution, described by Bushnell and Haas<sup>36</sup>, to which 1.5% Special Agar-Noble (Difco) was added when a solid medium was desired. The pH of the mineral solution was adjusted to 7.2 for the bacteria and 5.6 for the fungi prior to sterilization in an autoclave at 15 psi for 15 min. Alamac #1 and #2 were prepared and supplied by Monsanto Research Corporation, Dayton, Ohio. Each emulsion contained 97% (v/v) JP-4 jet fuel (supplier's data).

After sterilizing the mineral solution, 11 grams of Alamac #1 or Alamac #2, or 15 ml of filter-sterilized JP-4 jet fuel were added aseptically to each liquid system which contained 40 ml of a sterile salts solution. For solid media, 11 grams of Alamac #1 or Alamac #2 were mixed with 40 ml of warm mineral salts agar in a Waring Blendor. The mixture was dispensed to sterile Petri dishes and allowed to solidify.

## 2. Organisms

Pure cultures of four organisms isolated from fuel systems were used as test organisms. Two of them, *Pseudomonas aeruginosa* and *Hormodendrum* sp., were fuel-utilizers, and two, *Staphylococcus* and *Bacillus* spp., were nonfuel-utilizers. *Staphylococcus* and *Bacillus* spp. were tested for ability to survive in the emulsified fuel system. Fuel-utilizers were maintained in the mineral salts solution<sup>36</sup> with JP-4 as the source of carbon, and nonfuel-utilizers were maintained on Trypticase Soy Agar (TSA). Vegetative cells from bacterial cultures and spores and mycelia from fungal cultures were washed three times in sterile distilled water. The aqueous suspensions were then adjusted to a turbidity of 90% T in a Spectronic 20 colorimeter set at a wavelength of 550 mμ. Then 0.1 ml of bacterial cells or 1.0 ml of fungal spores and mycelia was used to inoculate each system.

Bacterial cultures were incubated at 37°C without shaking. Subsequently, bacterial growth was assayed by the plate count method using TSA. Fungal cultures were incubated at 26°C, and growth was determined qualitatively by visual observation for the presence of a mycelial mat.

## 3. Test Systems

Each emulsion was tested in several ways: (1) by mixing inoculum directly with the emulsion, (2) by overlaying liquid medium with the emulsions, and (3) by mixing the emulsions with mineral salts agar and preparing pour plates and streak plates.

## B. RESULTS

Microbial growth was not detected in or on either emulsion in the absence of the mineral salts solution. Liquid cultures of *Ps. aeruginosa* are shown in Figure 15. Visual inspection indicated that bacterial growth was limited to the aqueous phase, which is typical of such systems. Cultures containing Alamac #1 and Alamac #2 separated into three phases, while cultures containing JP-4 fuel remained in two phases.

Growth was complete after 3 days of incubation (Figure 16). System 4 (uninoculated) containing JP-4 fuel remained clear during the incubation period. A white flocculent turbidity developed in the aqueous phase of both uninoculated emulsion

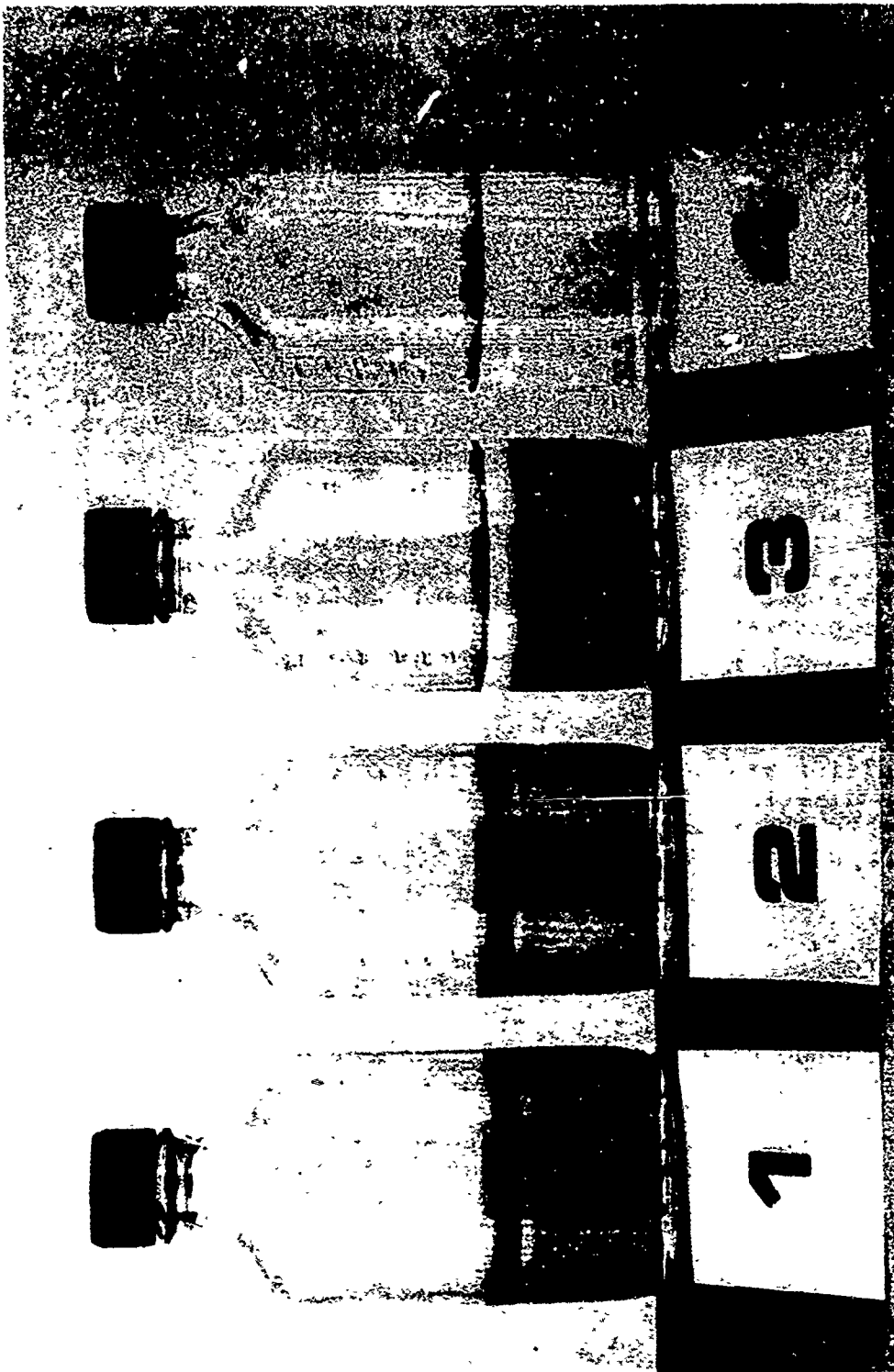


Figure 15. Cultures of *Pseudomonas aeruginosa* in Liquid Test Systems After 7 Days in Incubation.

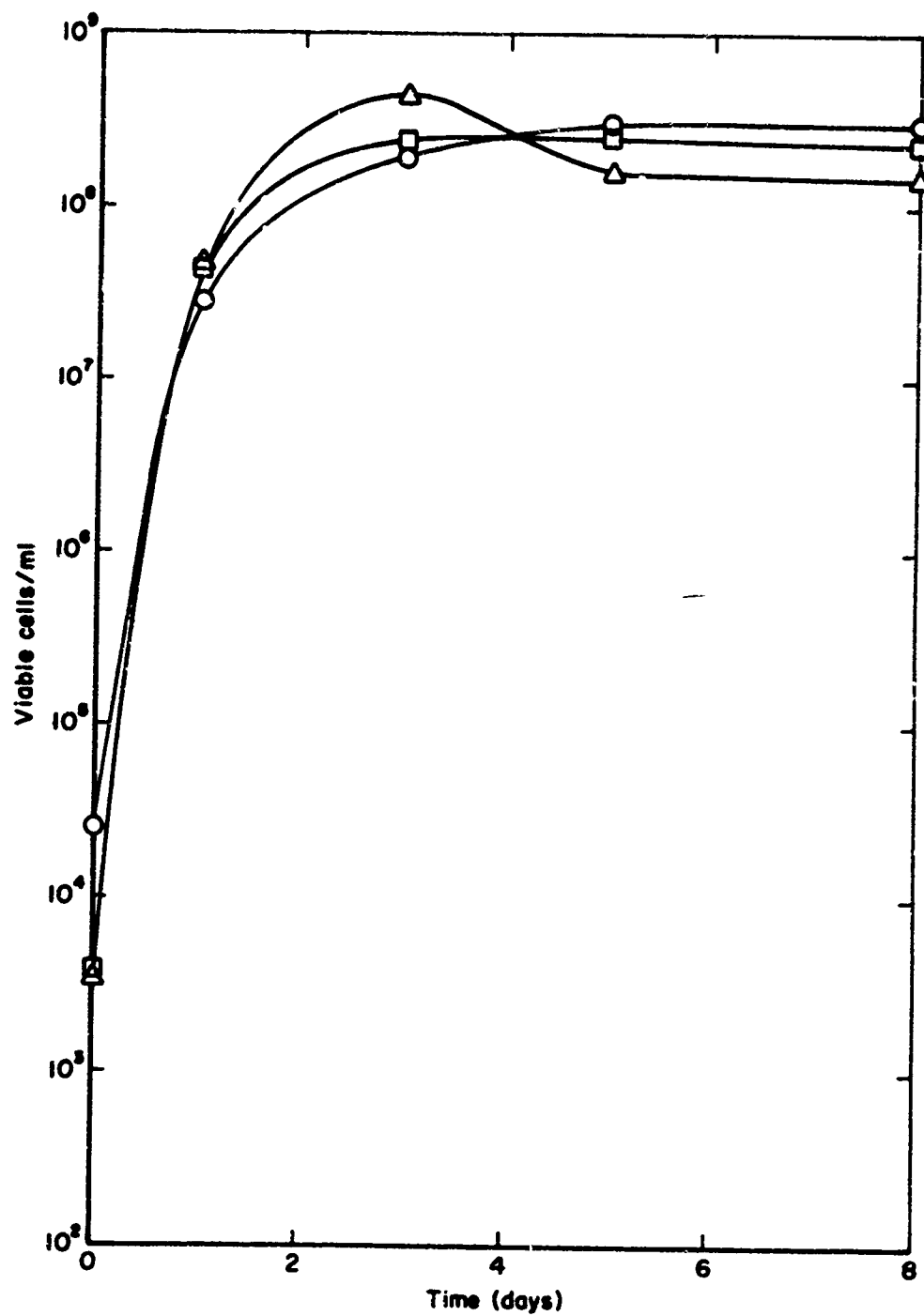


Figure 16. Growth Curves (Viable Cells) of *Pseudomonas aeruginosa* in Aqueous Phases of Test Systems.

systems, but this turbidity was easily distinguished from turbidity produced by bacterial growth. In each system, viable cells increased approximately 4 logs during the incubation period. No significant difference in rate or total amount of growth was noted among the three test systems.

Viable cells of a *Bacillus* sp. showed no significant increase after 4 days of incubation, and viable cells of the *Staphylococcus* sp. were not detected immediately after inoculation in either emulsion system. In the system containing JP-4 fuel,  $1.1 \times 10^5$  cells/ml were detected immediately after inoculation, but no cells were recovered after 4 days of incubation.

Due to the white flocculent precipitate that developed in liquid systems containing the emulsions, growth of the fungi could not be determined with certainty. However, a thick mycelial mat developed in the liquid culture containing JP-4 fuel. These data suggest that Alamac #1 and Alamac #2 may not support growth of the *Hormodendrum* sp. in a liquid system as well as JP-4 fuel. Therefore, the fungi were tested in solid media containing emulsion as the carbon source.

Growth of the *Hormodendrum* sp. on a solid medium is shown in Table XXXVIII. Due to the turbidity produced in a solid medium when emulsions were incorporated, fungal growth was difficult to detect. Good growth was noted on the spread plates of the systems with both emulsions, but growth was not as good in pour-plate cultures as in streak-plate cultures.

TABLE XXXVIII. GROWTH OF <i>HORMODENDRUM</i> sp. ON SOLID TEST SYSTEMS		
All plates received approximately the same inoculum		
	Pour Plate	Streak Plate
Alamac #1	+	++
Alamac #2	+	+++
JP-4 Fuel	++++	+++
+ = 1 to 10 colonies ++ = 11 to 20 colonies +++ = Intermediate ++++ = Confluent growth		



### C. DISCUSSION

In no case did we detect microbial growth in the absence of a water phase. Fuel-utilizing microorganisms did not grow in the fuel layer, but only in the aqueous phase or at the fuel-water interface. This is typical of our experience with such systems.

Bacterial growth in liquid systems containing Alamac #1 and Alamac #2 appears to be similar to growth in liquid systems containing JP-4 fuel. *Ps. aeruginosa* and the *Hormodendrum* sp. used in this study are stable fuel-utilizers and have been maintained by serial subculture in a mineral salts solution with JP-4 fuel for longer than 3 years<sup>38</sup>. This is not true of all fuel-utilizers. For example, Iizuka and Komagata<sup>40</sup> reported that certain pseudomonads lost their ability to assimilate hydrocarbon when cultured on nutrient agar slants.

Although our results suggest that the *Hormodendrum* sp. did not grow as well with fuel emulsions as carbon sources as they did with nonemulsified fuel, we feel that further work is needed. Poor growth of the fungus may be the result of the rapid rate at which fuel evaporated.

The responses of *Staphylococcus* and *Bacillus* spp. in media containing fuel emulsions did not differ from the responses of these organisms in similar systems containing nonemulsified JP-4 fuel.

Although rate and total amount of microbial growth were not significantly different in emulsion systems than in non-emulsion systems, the possibility cannot be excluded that products of microbial metabolism differed due to the presence of emulsifying agent(s).

### D. CONCLUSIONS

1. Alamac #1 and Alamac #2 inoculated directly did not support growth of fuel-utilizing organisms.
2. When either emulsion was used as the sole organic carbon source for a fuel-utilizing bacterium in an aqueous system, it supported abundant growth of fuel-utilizing organisms, but not of other organisms isolated from fuel. No significant differences were noted between emulsion cultures and cultures containing normal JP-4 fuel.

3. Emulsions also supported growth of a fuel-utilizing fungus on a solid medium. The data suggest that less growth was obtained with emulsions than with nonemulsified fuel, but more critical experiments are needed.
4. Two bacteria isolated from fuel systems, which do not grow on JP-4 fuel, showed no different survival curves in emulsion media than in JP-4 media.

APPENDIX VII. ALLISON T63 BENCH TESTS  
OF MODEL 250 FUEL SYSTEM COMPONENTS

A. FOREWORD

This report covers the test accomplished by Allison Division of G.M.C. to support the Monsanto effort in the USAAVLABS aircraft fuel system components; namely, a pump, control, and nozzle. Monsanto Research Corporation of Dayton, Ohio, furnished a test fluid comparable to JP-4 and a JP-4 emulsion, Alamac H26D. The purpose of the test was to furnish data for comparison with other emulsions.

B. SUMMARY

The fuel system components tolerated the emulsified fuel quite well, with only the fuel pump filter element showing a slight evidence of corrosion. Several other parts were discolored, but this was not thought to be detrimental.

The individual components retained their original calibrations after the emulsified fuel test.

Control metered flows were less with the emulsion as compared to the liquid fuel.

Fuel pump filter pressure drops ran considerably higher with the emulsion, resulting in bypassing action.

An estimated breakdown of the emulsion of 10% to 20% into liquid JP-4 at the control outlet was noted.

C. DISCUSSION

1. Test

The test was run in the Fuel Components Laboratory. The following T63-A-5 fuel system components, which were obtained from the Government Bond Room, were used.

P/N 6845577 Bendix Gas Producer Fuel Control S/N 191003  
P/N 6844544 Pesco Fuel Pump S/N PE130  
P/N 6842019 D.E.D. Fuel Nozzle S/N AGC-631

The primary test fluid used was Alamac H26D, a JP-4 emulsion prepared by the Monsanto Research Corporation and shipped to Allison in 55-gallon drums. This emulsion is a dispersion of JP-4 in ethylene glycol and water. The blend used on this test contained 97% JP-4, 1.35% water, 1.35% ethylene glycol, and 0.3% emulsifying agent by volume. The other test fluid used was MIL-F-7024A Type II, which is the equivalent of JP-4 and is used in the lab for all fuel system component testing.

Following procurement of parts, each component was disassembled and inspected, and selected pieces were photographed to establish the actual condition of materials as a baseline for evaluation of degradation effects of the emulsion. The parts were then reassembled.

The fuel pump and fuel nozzle were calibrated individually per the acceptance tests of their respective Engineering Design Specification (E.D.S.). The fuel control was run per the 10-point acceleration schedule defined in its E.D.S. MIL-F-7024A Type II test fluid was used on these preliminary calibrations. The parts were not required to conform to limits, since the results would be used strictly for a JP-4 vs emulsion comparison.

The components were then assembled as a system, and a baseline run was made on MIL-F-7024A Type II test fluid which consisted of the 10-point acceleration schedule on the fuel control. Black and white still photographs were taken at each point of the calibration as a means of measuring spray angle.

The next phase of the test was a repeat of the system run on JP-4 emulsion. The engine fuel pump inlet was connected to a Bell Helicopter Co. UH-1A helicopter ferry tank (P/N FCE-45624), which was furnished by Monsanto. The tank incorporated an internal electrically driven centrifugal boost pump. The pump (P/N RG 12240-2), which was made by Lear-Siegler, had current requirements of 28 volts and 3.75 amps and a rated speed of 7100 rpm. This pump was incapable of handling the emulsion. Pump voltage was varied to change pump speed, and the tank was pressurized to 0.5-in. Hg in an attempt to get the pump to function, but to no avail. Inspection of the pump revealed that the emulsion must pass through two 1/4 in. x 1-1/2 in. slots and then flow upward approximately 1/2 in. and pass through a 7/8-in.-diameter hole to get to the impeller. Due to its physical nature, it is felt that the emulsion would not flow through these restrictions, thus rendering the pump ineffective. A test equipment workhorse Ingersoll-Rand 50 gpm-3460 rpm centrifugal pump was substituted

and worked reasonably well; however, better results were obtained when the 55-gallon drum which contained the emulsion was pressurized to 2 psig. Black and white photographs were again taken at each point of the calibration. The emulsion flow rate was determined by a weight vs time method.

Following a soak period of 2-1/2 days, the components were each run individually per their respective E.D.S. on MIL-F-7024A Type II test fluid.

The components were then disassembled and inspected. The same pieces photographed prior to the test were rephotographed for comparison purposes.

## 2. Test Results

Figures 17 through 22 show various parts from the three T63 fuel system components prior to the test. Figures 23 through 28 show the condition of the parts after the test. The following visual observations were made:

- (1) Slight rust on the OD and ID of the fuel pump filter. Rust on the OD was concentrated at the ends of two pleats and was present prior to the test, but to a lesser degree.
- (2) Discoloration was noted on the fuel pump quill shaft (Figure 28), OD of spline end of pump drive gear (Figure 24), aft end of drive coupling, and OD of fuel nozzle valve cage. This discoloration did not occur on critical tolerance areas and had no effect on performance. For this reason it was not thought to be detrimental; however, extended testing would evaluate this better.
- (3) Dirt was in evidence throughout the fuel system, indicating that the fuel pump filter bypass valve had been open throughout at least a portion of the emulsified fuel run. This was further substantiated by the fuel pump filter drop pressures which were measured during the test.

Figures 29 through 32 show the fuel as it exited from the supply drum, test equipment boost pump, engine pump, and fuel control. The amount of free JP-4 increased as the fuel progressed through the system and was estimated to contain approximately 10-20% free JP-4 as it left the control. Some of this breakdown can be attributed to shear action and to

temperature induced by pumping action. Maximum temperature noted at the test equipment boost pump outlet was 135°F.

Figures 33 through 35 show the nozzle spray cone at 3 conditions while running the fuel system on MIL-F-7024A Type II test fluid.

Figures 36 through 38 show the nozzle spray cone at 3 conditions while running the fuel system on emulsified JP-4. Visually, no difference was noted in spray quality between the two fuels, but the spray angles were greater while flowing emulsion up to approximately 250 psi, and then lower up through approximately 500 psi. This is shown tabulated on data sheets AW.1200-00018 and AW.1200-00019, and is also present in curve form in Figure 39.

The individual component calibrations prior to and after the test are shown on data sheets AW.1200-00012 through AW.1200-00017. The calibrations compared favorably with the exception of the fuel pump filter bypass valve on which the leakage was out of limits after the soak period. The valve was removed for inspection, and it was found that a considerable amount of emulsified fuel with some entrapped dirt remained in the pump cavity. After cleaning out this residual fuel, the valve functioned as it had prior to the test.

Data sheets AW.1200-00018 and AW.1200-00019 are taken on the system runs. The control flowed from 0.5 - 28 pph leaner while flowing the emulsion. This is shown in curve form in Figure 40. The metering head ( $P_1 - P_2$ ) ran about 1 psi lower on the emulsion. On MIL-F-7024A Type II test fluid the pump filter pressure drop remained at zero, while on the emulsion it varied from 1.7 to 9.8 psi during the run with pressure instability at the higher levels, indicating that the bypass valve was opening. Normal bypass valve cracking pressure is 8 to 12 psig.

### 3. Disposition of Parts

Fuel system components were returned to the Government Bond Room in the "as is" condition.

Aircraft tank and remainder of emulsified fuel were held pending disposition instructions.

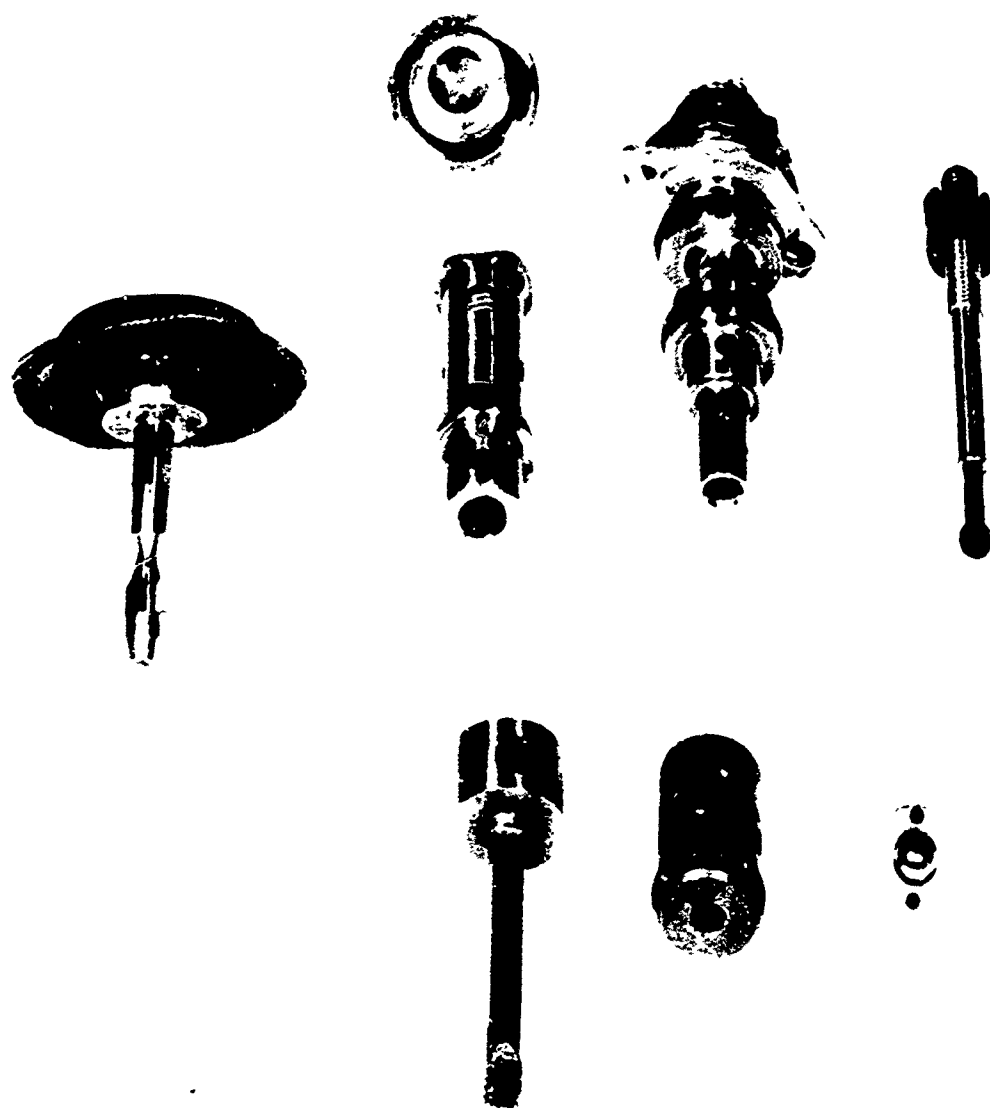


Figure 17. Fuel Control Prior to Test.

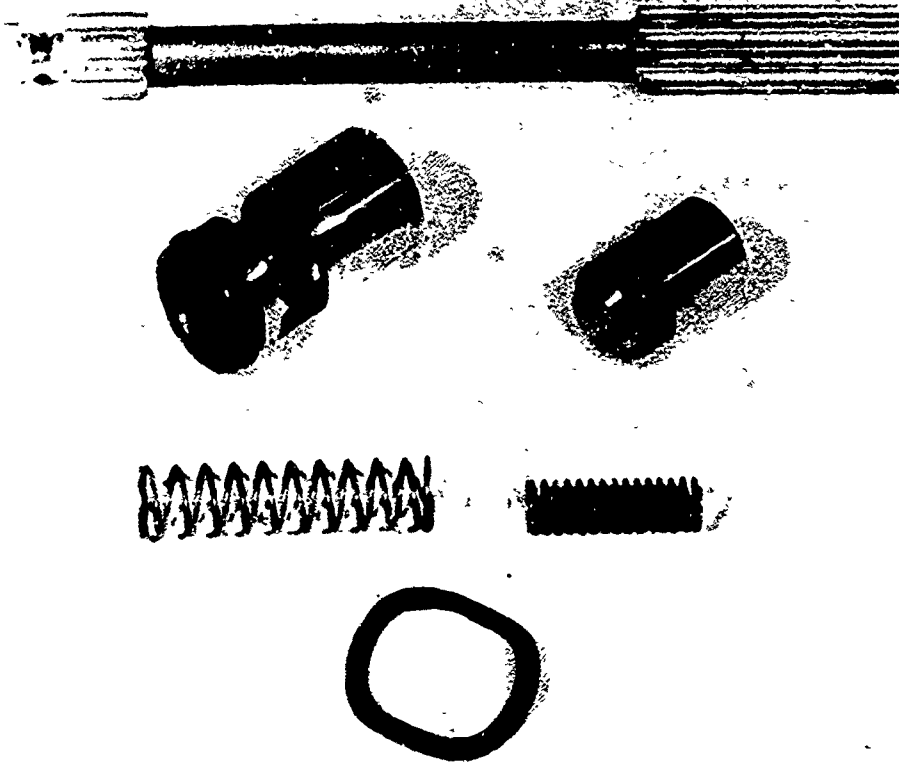


Figure 18. Pump Prior to Test.



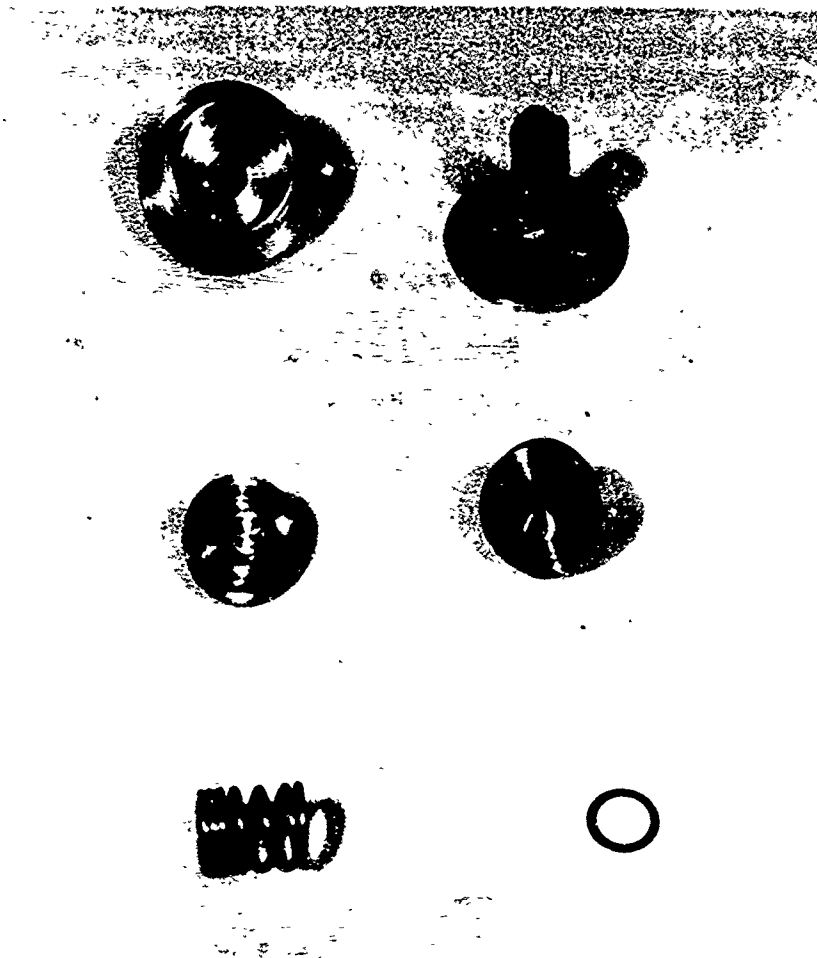


Figure 19. Fuel Nozzle Prior to Test.

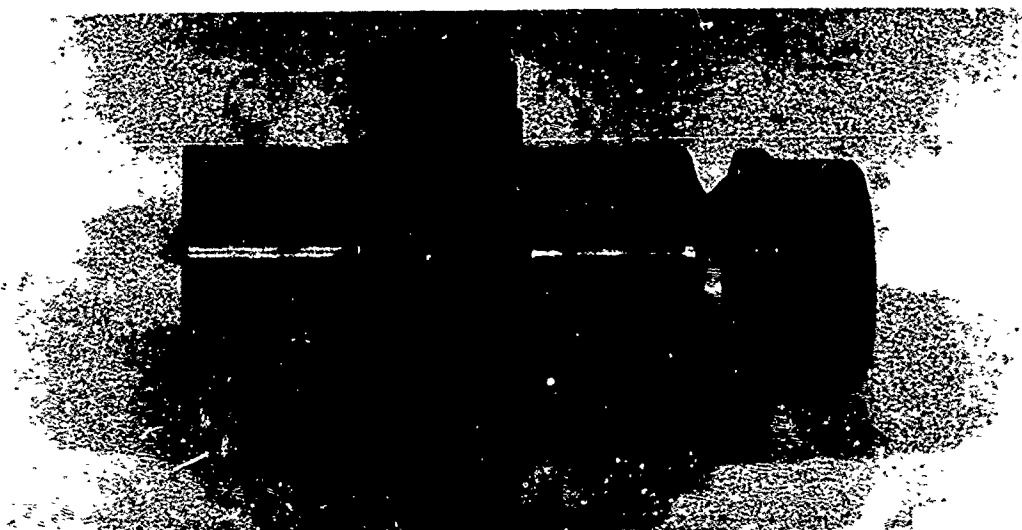
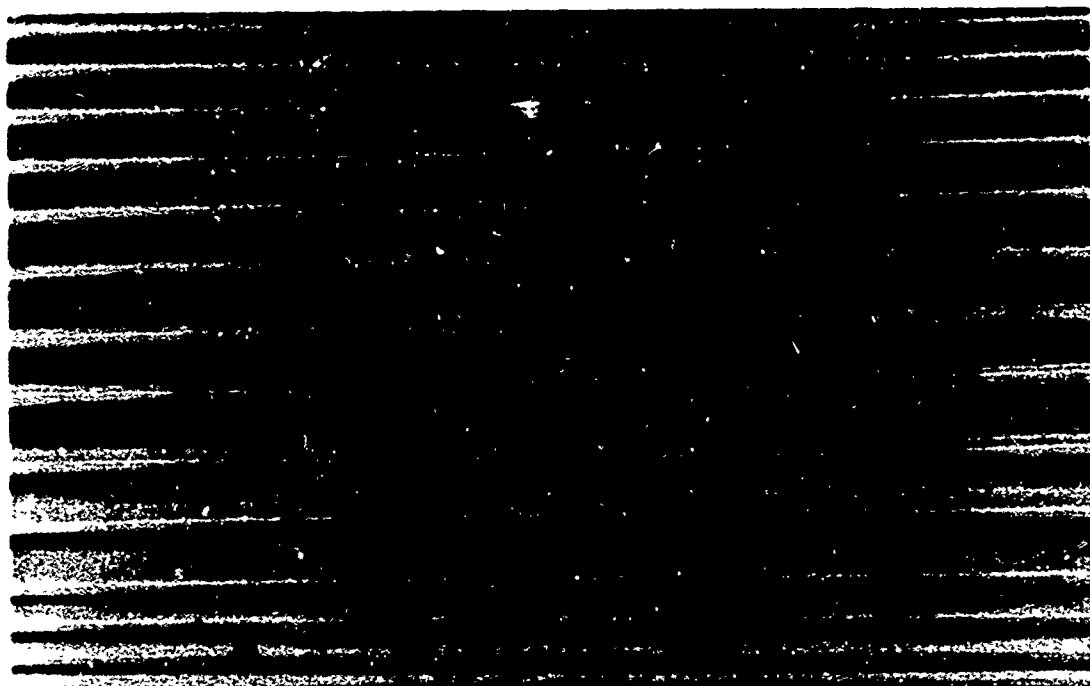


Figure 20. Fuel Pump Prior to Test.

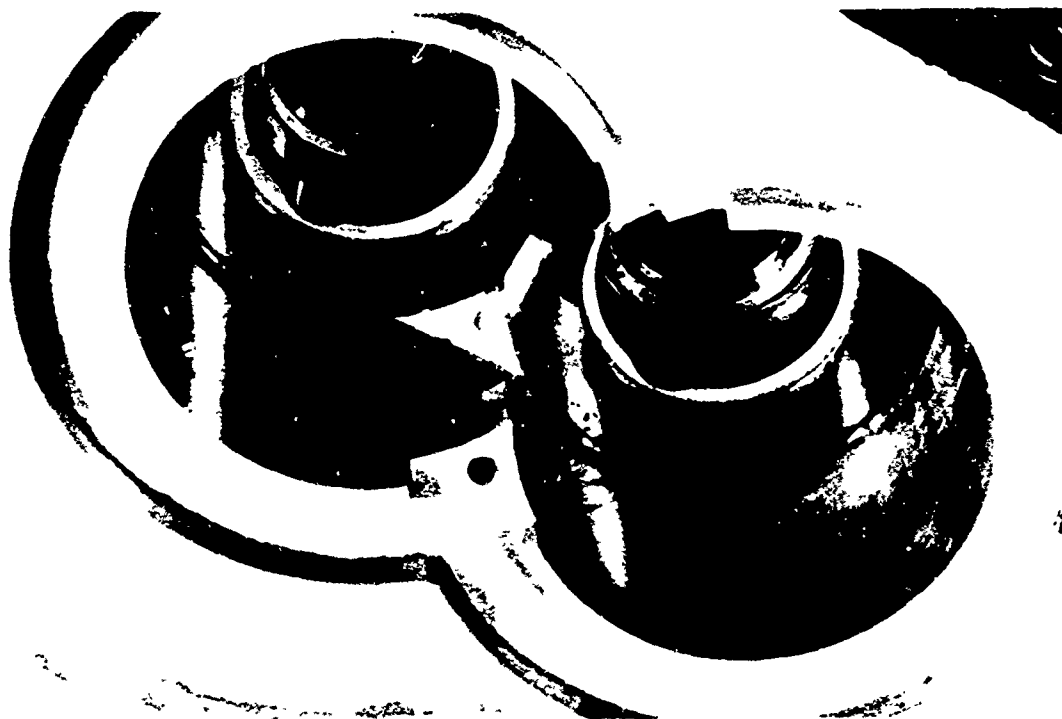
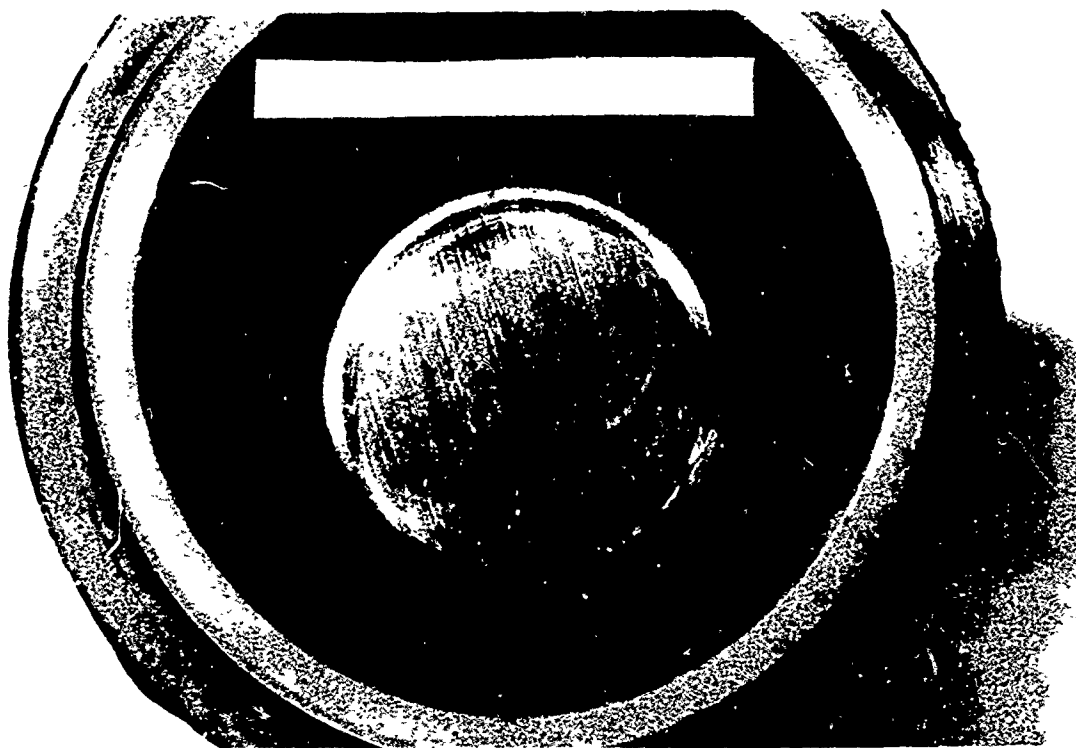


Figure 21. Fuel Pump Prior to Test.



Figure 22. Fuel Pump Prior to Test.

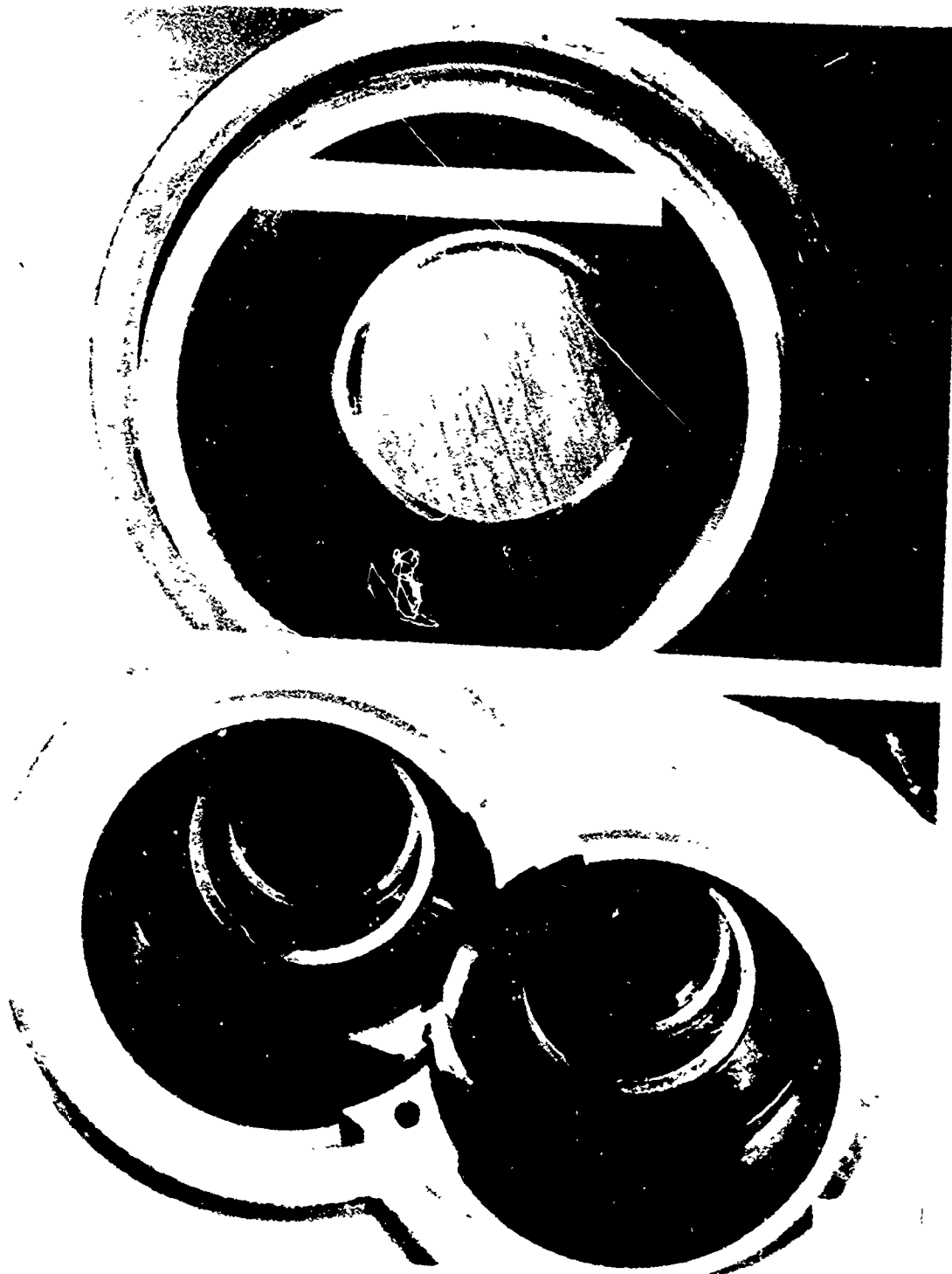


Figure 23. Fuel Pump After Test.

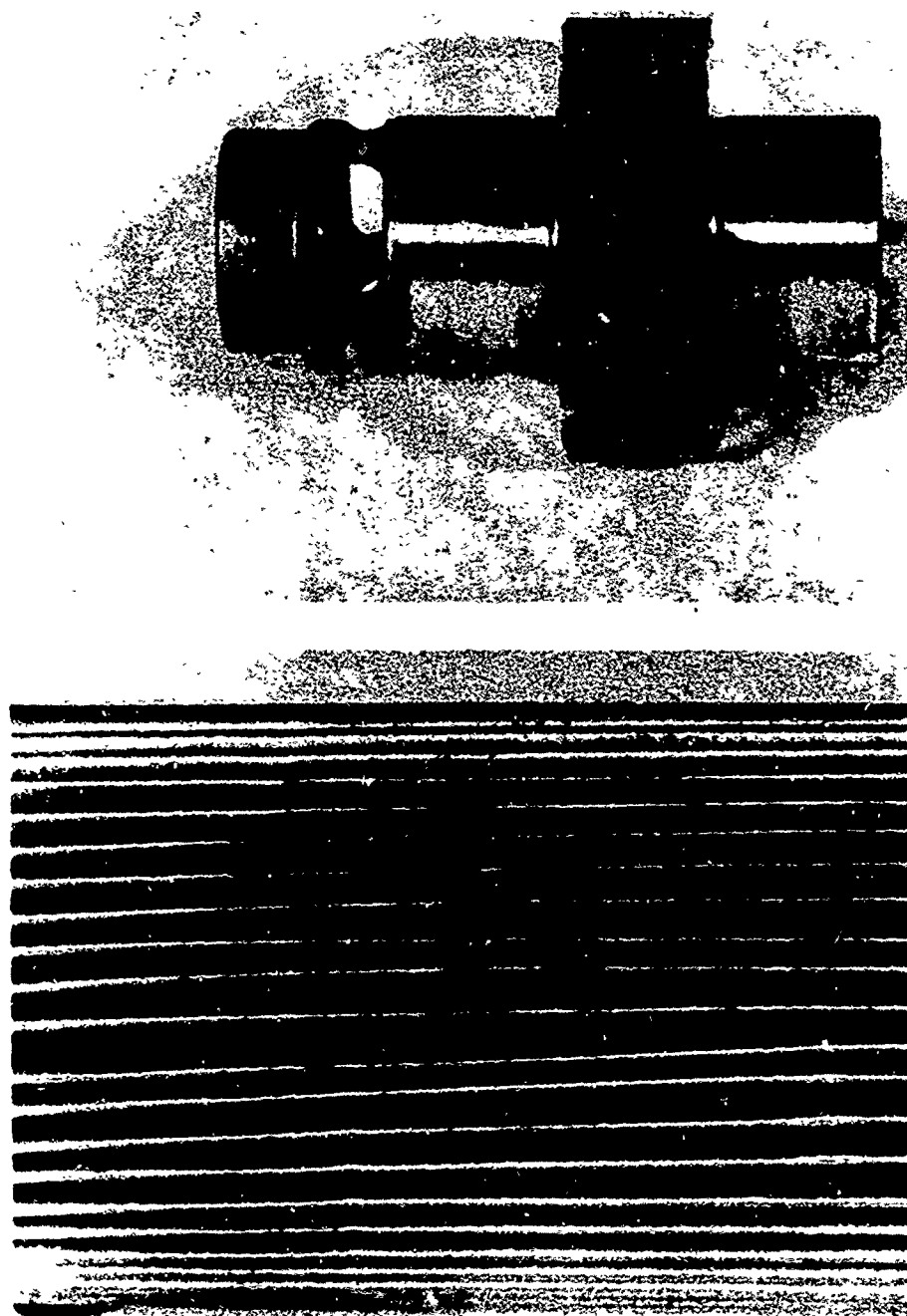


Figure 24. Fuel Pump After Test.



Figure 25. Fuel Nozzle After Test.

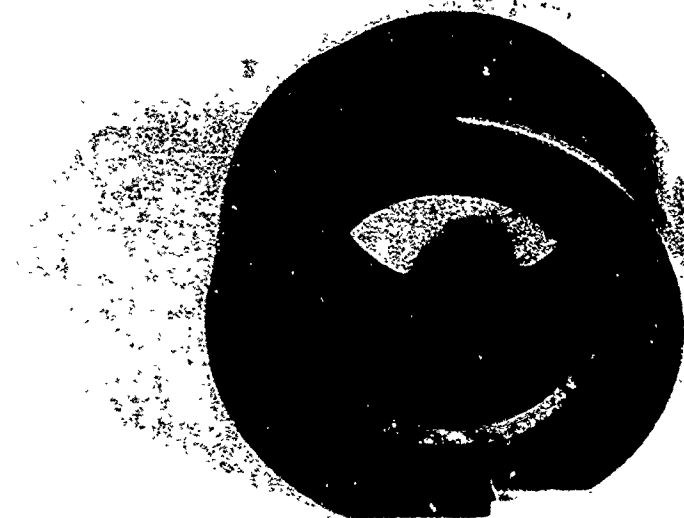
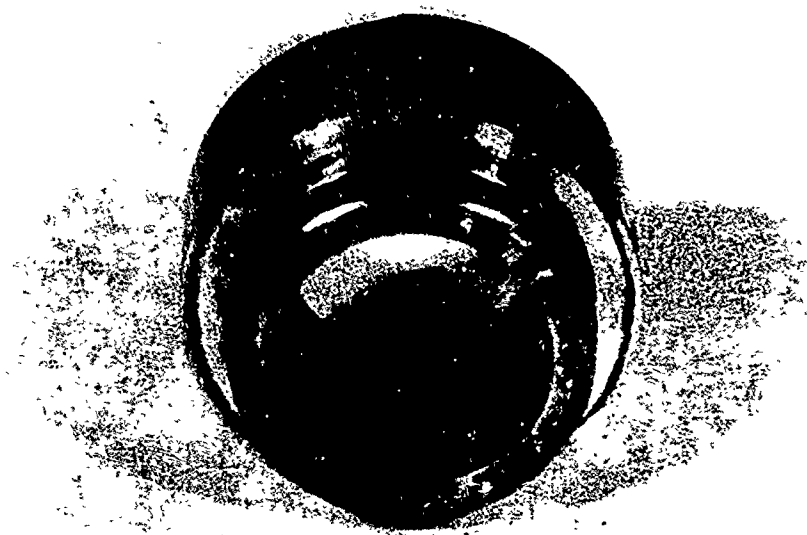


Figure 26. Fuel Pump After Test.





Figure 27. Fuel Control After Test.

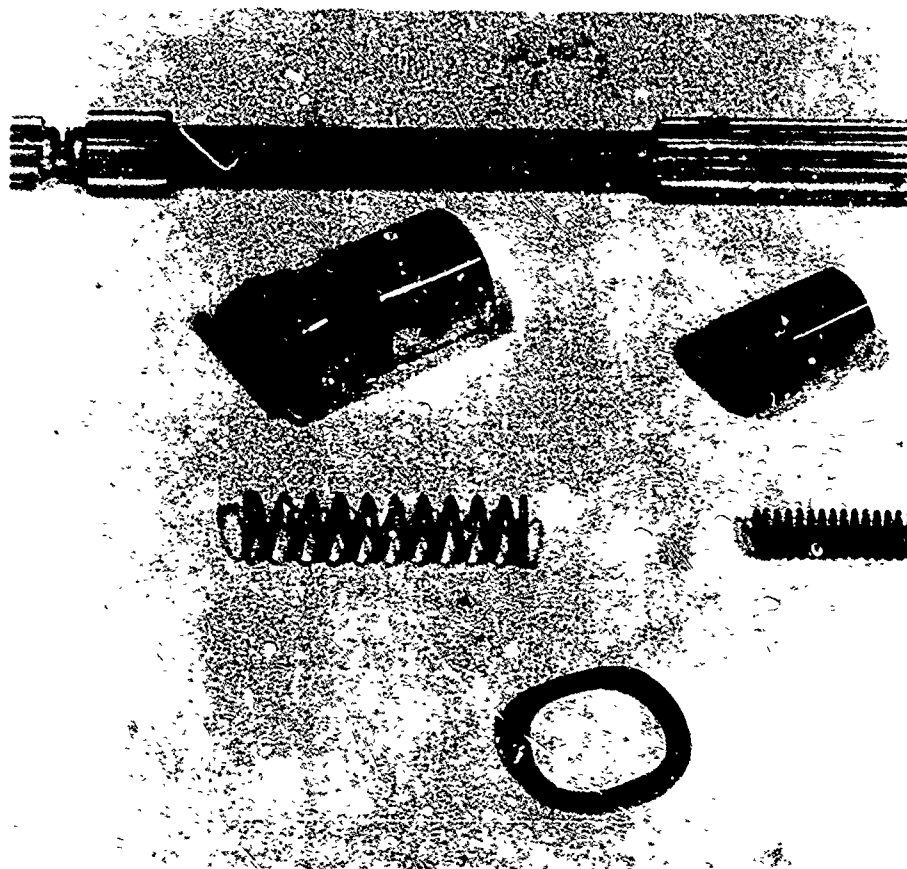


Figure 28. Fuel Pump After Test.



Figure 29. Supply Drum Outlet.

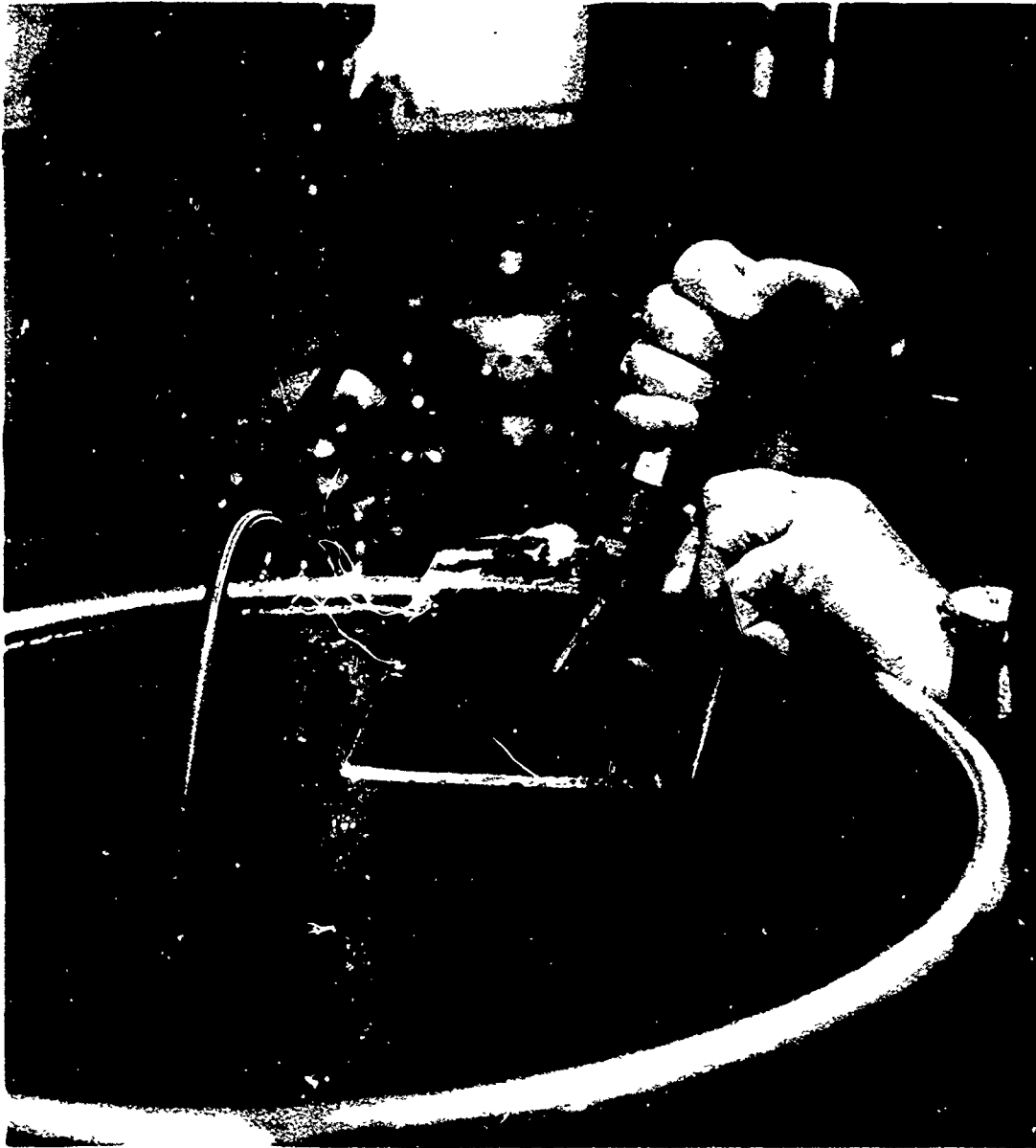


Figure 30. Fuel Pump Inlet.



Figure 31. Fuel Pump Outlet.

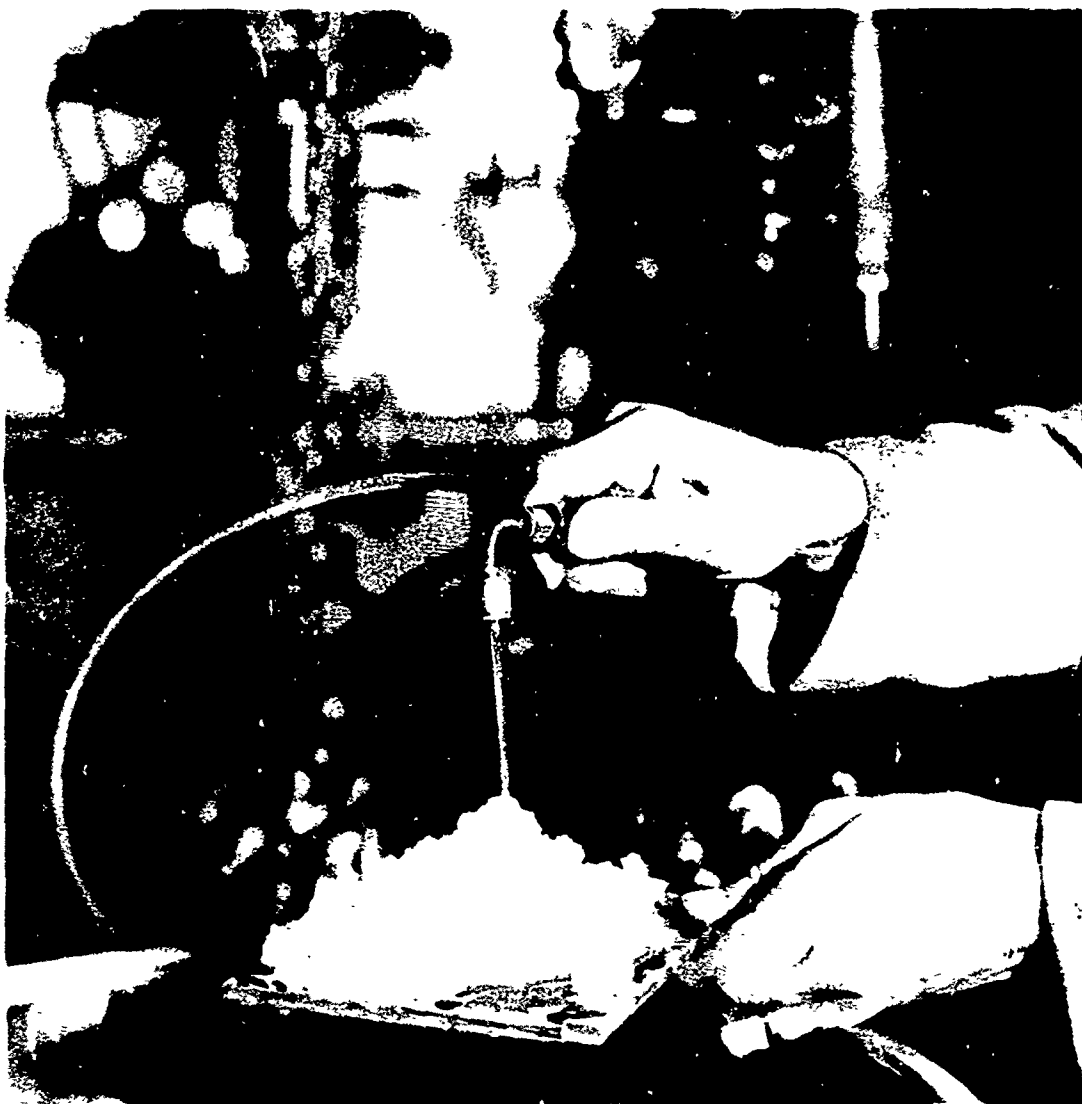


Figure 32. Fuel Control Outlet.



Figure 33. Spray Cone of MIL-F-7024A Type II  
Test Fluid - 32.6 PPH.

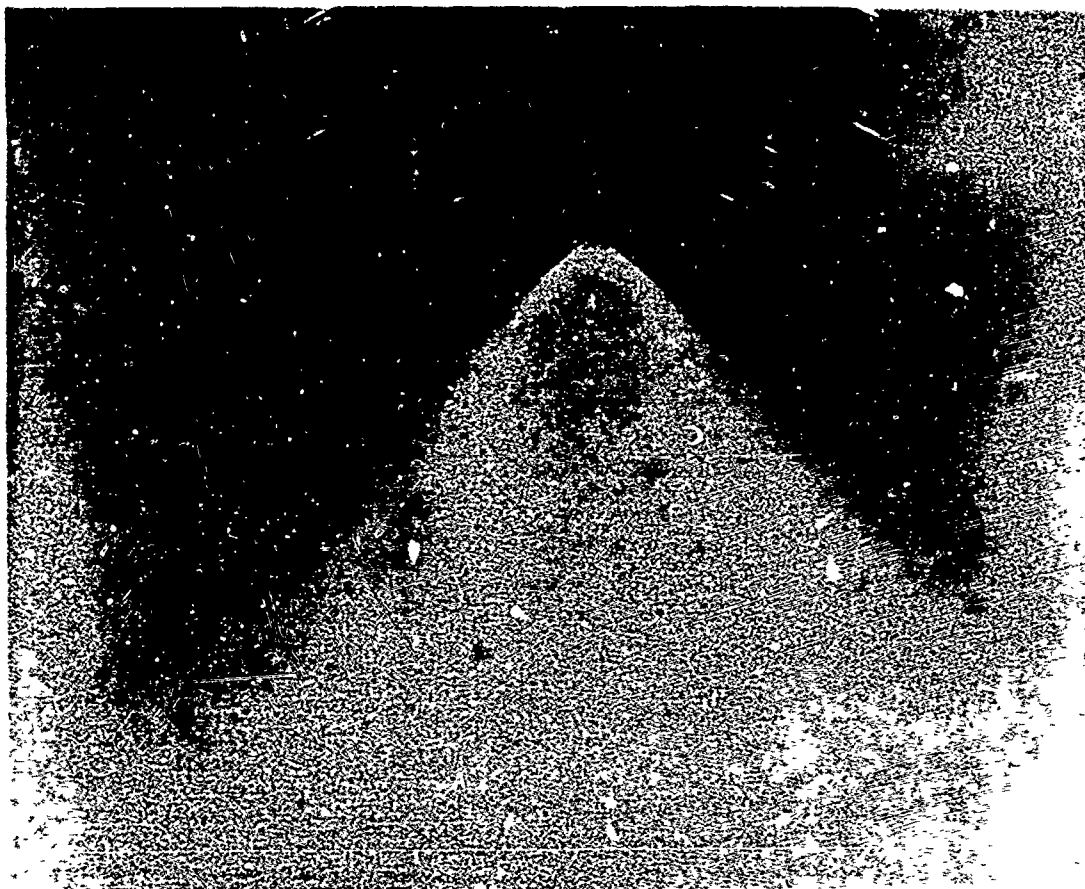


Figure 34. Spray Cone of MIL-F-7024A Type II  
Test Fluid - 148.7 PPH.





Figure 35. Spray Cone of MIL-F-7024A Type II  
Test Fluid - 254.7 PPH.



Figure 36. Spray Cone With Alamac Emulsion - 32.1 PPH.



Figure 37. Spray Cone With Alamac Emulsion - 132.7 PPH.

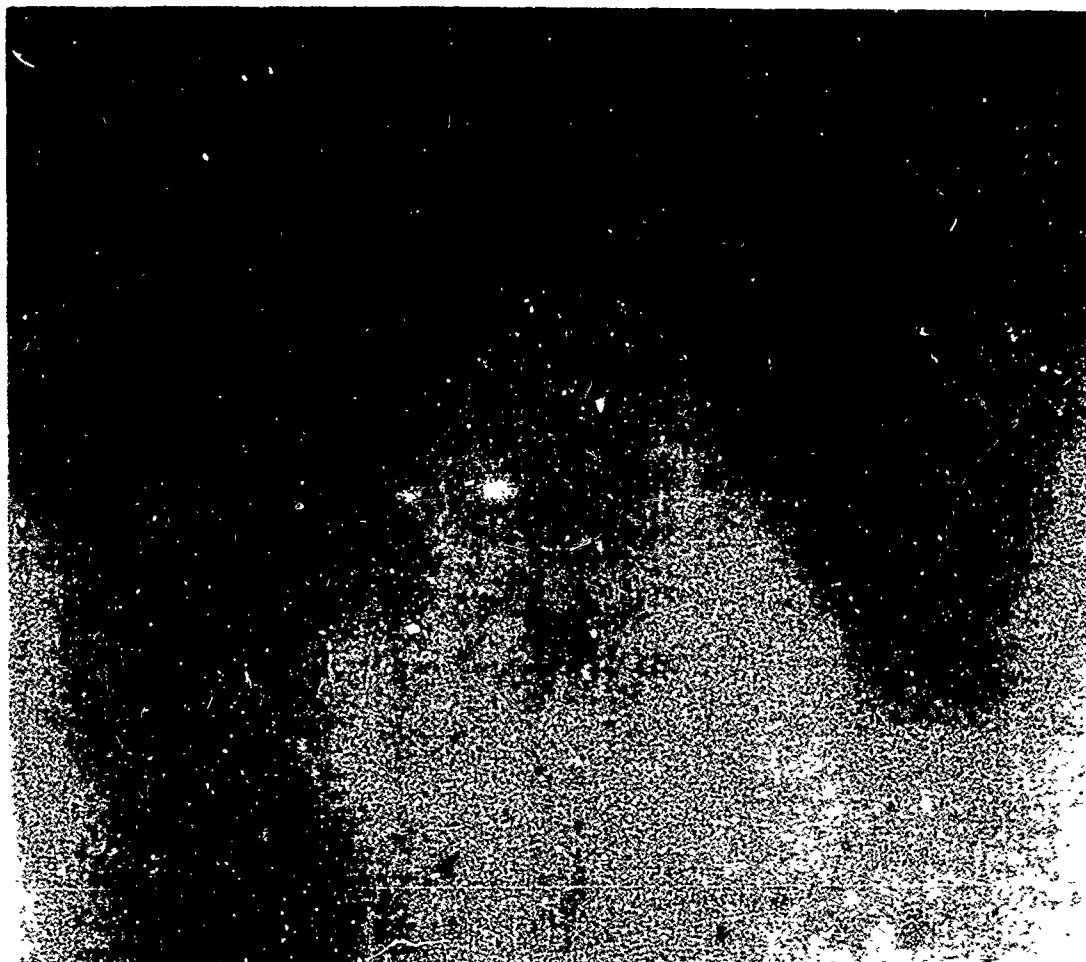


Figure 38. Spray Cone With Alamac Emulsion - 226.6 PPH.

AW-2030

PARTS TEST LABORATORY DATA SHEET

TEST LOCATION RCI CHARGE NO AW120003-SOL PROJ NO E-67033 DATE 3-10-67 FILE NO 10534B

TEST PLANT MTL-P-7084A-11 ROOM NO 56 SERIAL NO 8045

PART NAME & NO 563 Fuel Pump P/N 6844544 OBSERVED BY AT

TITLE OF TEST Acceptance Test per E.D.S. 1219 Rev. C Initial Calibration

No.	Part	Inlet	Disch	Flow	Leakage	Rev. Mod.	Boost
		PSIA	PSIG	PPH	GPM	cc/min	Flow
<b>4.4 Calibration</b>							
1.	624	3	14-15	130	0.4	0	PSI GPM
2.	3719	50	"	600	995.7	0	PSI GPM
3.	3719	50	"	150	1014.7	0	PSI GPM
<b>4.5 Leakage</b>							
3719	-	14-15	900	-	0	0	PSI GPM
<b>4.5.1 Valve Reverse Leakage</b>							
-	-	-	600	-	-	2.2	Limit 300 cc/min max.
<b>4.5.2 Filter Ry-Res Valve Leakage</b>							
-	-	7	-	-	-	4.6	Limit 100 cc/min max.
<b>Note:</b> Under any condition of operation during Acceptance Testing the maximum permissible leakage from the drain port shall be 0.5 cc/min. There shall be no external leakage from the splitlines, holes or castings.							

PL 2524100-1

ENGINE SPEC.										FUEL										AIR FORCE										CUSTOMER ALLISON										CHARTER SPEC.																													
MODEL DP-03 (A1-L2)										FLOW BENCH NO. 54										OPERATOR RICE										TEST SPEC. 0 3612										LIMIT FOR ALL BENCHES										SERIAL NO. 191 003										SHEET NO. 1 of 1									
PARTS LIST										DATE 3 0-67										SHIFT 2																																																	
TEST SPEED										7% PSIA PSIG										7% PSIA PSIG										7% PSIA PSIG										7% PSIA PSIG																													
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NOTATION GOV AS VIEWED FROM SHUNT END.										INITIAL CALIBRATION										CONNECTIONS																													
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NOTE: 1. Set test conditions in the following sequence: (1) P<sub>5</sub>, (2) Wt Speed, (3) Fuel Supply, (4) P<sub>2</sub>.  
2. Fuel Supply not to exceed 150 PPM @ 600 RPM, P<sub>1</sub> w'ng test cond. of I.P. 1.3 sec.  
3. Set 1<sup>st</sup> Ag. Pr-Pg while running these points.

PARTS TEST LABORATORY DATA SHEET

PAGE \_\_\_\_\_ CHARGE NO. AW-1200-13-501 PROJ NO. E67033 DATE 3-10-67 FILE NO. 10548  
 TEST LOCATION: FCL ROOM NO. 50 BENCH COX  
 TEST FLUID: MIL-R-7024A II OBSERVED BY: \_\_\_\_\_  
 PART NAME & NO: 250 FUEL NOZZLE IN 5842019 SERIAL NO. AGC-631  
 TITLE OF TEST: CALIBRATION PER E.D.S. 1225A INITIAL CALIBRATION

NOZZ. NOSE NOSE: _____ SPRAY									
INITIAL ROTO FLOW TEST FLOW SPRAY ANGLES									
PSIG	PPH	PPH	PPH	PPH	PPH	PPH	PPH	PPH	PPH
1	2	3	4	5	6	7	8	9	10
50	26.4	24.6	22.8	28.4	95	80-100			
100	25.3	35.1	37.3	39.9	83	72-92	112	108	123
125	43.3	42.5	45.5	50.5	73	70-90			
200	119.9	102.6	118.6	125.4	87	75-95	120	118	121
300	180.0	160.2	172.9	195.8	95	83-103			
400	233.0	203.4	221.4	248.6	92	84-104	133	117	121
500	122.9	124.2	124.2	124.2	124.2	124.2	124.2	124.2	124.2
125	45.2	46.5							
600									
200-5									
4C									

AW-1200-00014

PARTS TEST LABORATORY DATA SHEET

PAGE 1 CHARGE NO AW-1200-13-501 PROJ NO F 62033 DATE 3-16-67 FILE NO PE 130  
 TEST LOCATION FCL ROOM NO 8045 BENCH AT  
 TEST FLUID MIL-P-7024A-II OBSERVED API 68.4544  
 PART NAME & NO T63 Fuel Pump P/N 68.4544 SERIAL NO PE 130  
 TITLE OF TEST Acceptance Test per E.D.S. 1219 Rev. C AFTER EMULSIFIED FUEL TEST

Boost										Boost Disch	
E.D.S. Pump		Pr. Inlet Disch		Leakage		Rev. Fed.		Rise Plom		Rise Plom	
Section		Pr. Inlet		Seal		L'kg. L'kg.		PSI		PSI	
No.		PSIA		PPH		GPH		PPH		PPH	
4.4 Calibration											
1.		14-15		139		0.4		0		0	
2.		50		600		1009.3		0		0	
3.		50		150		1034.7		0		0	
4.5 Leakage											
3719		14-15		500		-		0		-	
4.5.1 Valve Reverse Leakage											
-		-		600		-		-		-	
4.5.2 Filter By-Pass Valve Leakage											
-		7		-		-		-		-	
-		-		-		-		-		-	
-		-		-		-		-		-	
-		-		-		-		-		-	
Note: Under any condition of operation during Acceptance Testing the maximum permissible leakage from the drain port shall be 0.5 cc/min. There shall be no external leakage from the splitlines, holes or castings.											



## TEST SPECIFICATION SHEET

**REDEX PRODUCTS AEROSOL**

INCORPORATED / SOUTHERN BELL

15:1 6:750.7

[illegible]

NOTES: 1. Test conditions in the following sequence: (1) Pc, (2) M1 Speed, (3) Fuel Supply, (4) P2.  
2. Fuel supply not to exceed 150 PPH Q 600 P91, P1 using test cond. of I.P. 1.3 Sec.  
3. Set 1<sup>st</sup> Ag. Pr-Pg while running these points.

AW-1439

PARTS TEST LABORATORY DATA SHEET

CHARGE NO. AW-1200-13-501 PROJ NO. E 67033 DATE 3-16-67 FILE NO. 10548  
 TEST LOCATION FCL ROOM NO. 50 MENCH COX SERIAL NO. AGC-631  
 TEST FLUID MIL-P-7024A II OBSERVED BY AT  
 PART NAME & NO. 250 FUEL NOZZLE P/N 1225A AFTER 2 FUEL TEST

TITLE OF TEST CALIBRATION PER E.D.S. 1225A

Inlet Pr.	PSIG	Nozz. Nozzle Nozzle		Spray Angle Limit	1	2	3	4	5	6	Diff CC	Diff %	Max. Limit
		Flow Min	Flow Max										
60	26.45	24.6	27.9	28.4	88	80-100							
100	35.4	35.1	37.4	39.9	80	72-92	110	118	119	117	13	10.6	30%
125	42.75	42.5	45.0	50.5	83	70-90							
200	116.0	102.6	115.4	125.4	84	75-95	116	114	119	123	17	13.0	20%
300	178.0	160.2	178.0	195.8	86	83-103							
400	223.0	203.4	221.4	248.6	84	84-104	129	122	124	140	22	15.3	15%
200	123.0	122.9	122.9	122.9	84	84-104	129	122	124	140	22	15.3	15%
125	43.7	46.0	46.0	46.0	84	84-104	129	122	124	140	22	15.3	15%
600													
200-5													
40	17.2	18.8	18.8	18.8									

AW. 1200-00018

98-2463

PARTS TEST LABORATORY DATA SHEET

CHARGE NO. AW. 1200-13-501 WJ MC R-67233 DATE 3-14-67 FILE NO. 1054B  
 TEST LOCATION Fuel Components Lab. ROOM NO. 56 BENCH  
 TEST FLUID ALAMAC H260 EMULSION OBSERVED BY AL  
 PART NAME & NO. AL SERIAL NO. ---

TITLE OF TEST Bench Test of T-63 Fuel System Components on Monsanto Deulsified JP-4

Test Pt.	Speed RPM	Thro. DEG	Pc. PSIA	W2 PSI	Nozzle Flow		Pump Inlet		Pump Filter		Spray Angle	
					Wt. LBS.	Time Min/Sec	PPH	PSIO	PPH	PSIO		4P. PSI
2.1	600	W0	14.7	7.0	.535	1:00	32.1	20	12	1.72	32	105
3	1500	"	19.0	11.0	.647	1:00	38.8	19	23	2.95	32	96
3	2575	"	34.0	15.0	1.042	1:00	62.5	17	31	5.06	33	92
4	2800	"	39.0	16.5	.659	0:50	79.1	15	32	5.57	33	93.5
5	3200	"	50.0	25.0	1.106	0:30	132.7	10	30	7.6	33	96
6	3600	"	63.5	30.0	.792	0:15	190.1	5	30	5.25	33	95
7	4000	"	73.0	33.5	.899	0:15	213.4	1	36	9.82	33	96
8	4200	"	88.0	40.0	.944	0:15	226.5	0	28	9.82	33	92.5
9	3600	"	63.5	37.0	.780	0:15	167.2	10	34	9.32	32	95
10	1500	"	19.0	12.5	.633	1:00	38.0	11	8	5.69	32	95
P/N 6845517 Fuel Control S/N 191043												
684544 Fuel Pump P2130												
6842019 Fuel Nozzle AQ031												

P/N 6845517 Fuel Control S/N 191043  
 684544 Fuel Pump P/N 20  
 6842019 Fuel Nozzle M/C 31

179

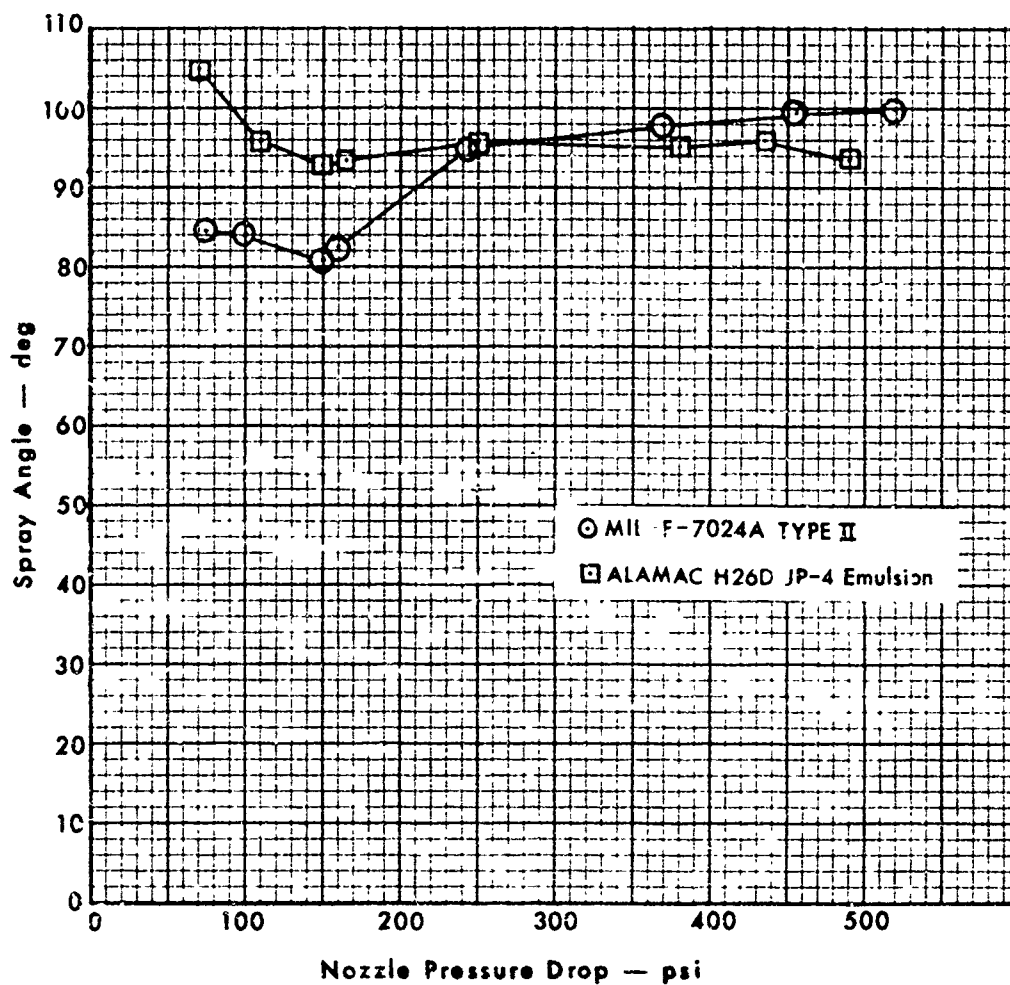


Figure 39. T63 Bench Test of Alamac Emulsion.  
Spray Angle vs Nozzle Pressure Drop.

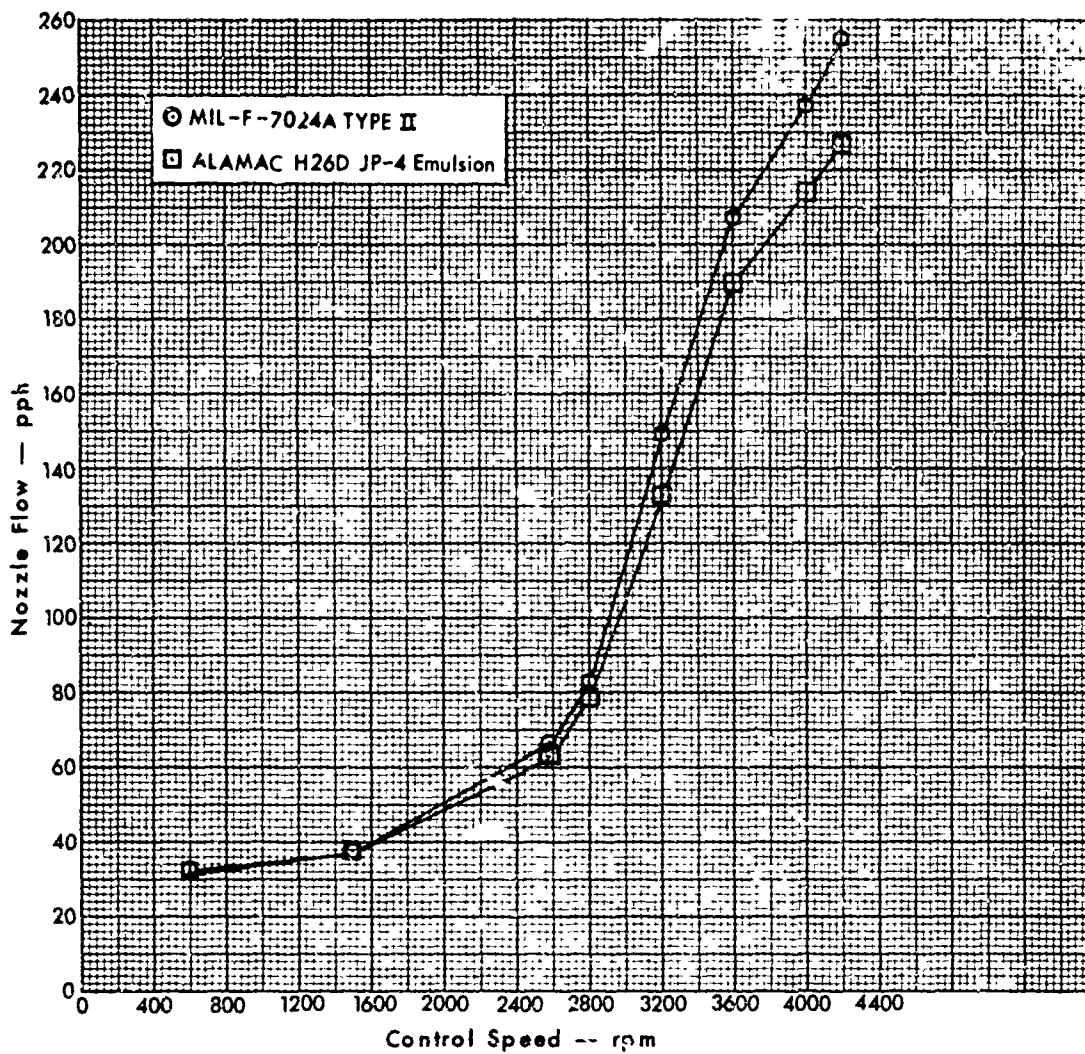


Figure 40. T63 Bench Test of Alamac Emulsion Acceleration Schedule.

UNCLASSIFIED

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11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY U. S. Army Aviation Materiel Laboratories Fort Eustis, Virginia 23604
13. ABSTRACT The objective of this contract was the development of flammability-controlled JP-4 emulsions for use in gas turbine engines and recovery of JP-4 from the emulsified fuel for forward base usage. Such emulsified fuels were designed to reduce the probability or intensity of in-flight or postcrash fires. The Alamac emulsion produced under this contract reduced the flame propagation rate to 1/87th that of JP-4 and reduced the area of dynamic burning to 1/6th that of JP-4. Other flame and explosivity tests also showed lower flammability. The emulsion was stable over a -40° to 160°F range, and exhibited no sensitivity to impact, vibration, or gravity acceleration values up to 10,000 g's. Emulsion viscosity met contract requirements, exhibiting yield stress values of about 1300 dynes/cm <sup>2</sup> . Tests with metals and elastomers used in fuel systems showed negligible or low emulsion effect. Lubricity tests showed the emulsion to have a coefficient of friction considerably lower than JP-4 alone. Negligible static charge buildup and high conductivity significantly lowered this potential hazard for the emulsion. Although the emulsion can be pumped satisfactorily, it does not flow freely to a sump. The Alamac emulsion can very readily be broken chemically: The raw recovered JP-4 contains the emulsifier which can be removed quantitatively by filtration through a column of attapulgite clay. Emulsion partially broken by thermal extremes or by multipassage through a centrifugal pump can be reconstituted by mild agitation. Six hundred gallons of the emulsion were produced using a standard formula and procedure.		

DD FORM 1473

REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Aviation Fuel						
Emulsions						
Fuel Emulsions						
JP-4						
Emulsifiers						
Surfactants						
Safety						
Flammability						
Explosivity						
Thermal Stability						
Gas Turbine Fuel						
Tallow Amine Acetate						
Fuel Separation						
Gravity Acceleration						

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